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THE SURFACE TENSION AND TRANSITION TEMPERATURE  
DEPRESSION IN LIQUID HELIUM SYSTEMS

BY



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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled THE SURFACE TENSION AND TRANSITION TEMPERATURE DEPRESSION IN LIQUID HELIUM SYSTEMS, submitted by Wytze Brouwer, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.



ABSTRACT

A theory of the surface tension of a quantum liquid, proposed by Atkins, is developed further and applied to liquid helium at 0°K. On the basis of the imperfect-gas model developed by Gross and Pitaevski the free energy per unit area arising from the density non-uniformity is calculated. This surface free energy is then identified with the "intrinsic" surface tension of liquid helium.

The same model of the surface tension of a quantum fluid is then used to calculate the interfacial surface tension in a phase-separated  $\text{He}^3$ - $\text{He}^4$  system at  $T = 0^\circ\text{K}$ . The result obtained is then contrasted with the corresponding result based on a "classical" model of the surface tension of an ideal fluid. A corresponding experimental study should be able to distinguish quantitatively between the two predictions.

We also discuss the effect of density non-uniformities on the lambda transition in  $\text{He}^4$  films. Semi-quantitative evidence is obtained that the lambda temperature depression in  $\text{He}^4$  films is, at least in part, due to the presence of excitations at the free surface of the film.

We also obtain an estimate of the lambda temperature depression in rotating helium as a function of both the angular speed of rotation and the physical dimensions of the container. The result obtained is more general than, and under special conditions reduces to, the previous results obtained by Andronikashvili, Mamaladze and co-workers.



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## CHAPTER 1

### INTRODUCTION

The study of liquid helium is of considerable physical interest because it is the only liquid that exhibits quantum effects on a macroscopic scale. Before we delve into the study of certain specialized problems concerning this liquid, it appears worthwhile to give a brief outline of some of its important properties that arise by virtue of these quantum effects.

Kamerlingh Onnes (1) was the first to successfully accomplish in 1908 the liquefaction of helium. He discovered that the critical temperature of helium was about  $5.2^{\circ}\text{K}$ , and its normal boiling point about  $4.2^{\circ}\text{K}$ . Solid helium, however, could not be obtained simply by cooling the liquid. Owing to the large zero-point energy of the helium atoms (which arises from their light mass) and the relatively weak interatomic attractive forces (which are so because of the closed structure of the helium atoms), the solid phase can be obtained only by applying an external pressure of at least 25 atmospheres even at  $T = 0^{\circ}\text{K}$ .

As early as 1911, Kamerlingh Onnes (2) noticed that strange things happened to liquid helium when it is cooled below about  $2.2^{\circ}\text{K}$ . As the temperature is decreased below this value, the liquid, instead of continuing to contract, began to expand. This suggested to Keesom and Wolfke (3) the possibility of helium undergoing an allotropic modification at  $T \approx 2.2^{\circ}\text{K}$ ; they



designated the liquid at lower temperatures as HeII and that at higher temperatures as HeI.

The discovery that gave this transition the name  $\lambda$ -transition was due to Keesom and Clusius (4) who found in 1932 that while the phase transition at  $2.18^\circ\text{K}$  was not accompanied by a latent heat, it was indeed accompanied by a singularity in the nature of the specific heat curve, whose shape resembled the greek letter lambda. Recent measurements, by Fairbank, Buckingham and Kellers (5), of the specific heat at saturated pressure have shown that, as the temperature approaches  $T_\lambda$ ,  $c_{\text{sat}}$  diverges in the manner of the logarithm of the magnitude of the temperature interval  $|\Delta T_\lambda| \equiv |T - T_\lambda|$ . For the temperature interval  $10^{-6} \leq |\Delta T| \leq 10^{-2}$ , the specific heat satisfied the empirical formula:

$$c_{\text{sat}} = 4.55 - 3.00 \log_{10} |\Delta T| - 5.20\delta \frac{\text{joule}}{\text{gm } ^\circ\text{K}}, \quad (1.1)$$

where  $\delta = 0$  for  $T > T_\lambda$ , and  $\delta = 1$  for  $T < T_\lambda$ . It is clear that there occurs a discontinuity in the specific heat of the amount

$$\Delta c_{\text{sat}} = c_{\text{sat}}(T > T_\lambda) - c_{\text{sat}}(T < T_\lambda) = -5.20 \frac{\text{joule}}{\text{gm } ^\circ\text{K}}. \quad (1.2)$$

A closely related property of liquid helium was discovered by Keesom and Miss Keesom in 1936. They noticed that as liquid helium passes through the  $\lambda$ -point into the helium II phase there occurred an enormous increase in its thermal conductivity.

Earlier in 1930, Keesom and van den Ende (6) discovered, rather accidentally, one of the most important properties of





liquid helium. They observed that liquid helium, when cooled below  $2.18^{\circ}\text{K}$ , could manage to escape through extremely tiny leaks in the apparatus which had been completely leakproof at higher temperatures to both helium I and gaseous helium. This observation seemed to indicate an enormous drop in the viscosity of the liquid on passing down through the lambda point.

Early measurements on the viscosity of liquid helium, however, yielded conflicting results. Experiments based on the oscillating disc method (7) showed that the viscosity of helium II, though it decreases continually with decreasing temperature, is not very different from the viscosity of helium I. On the other hand, experiments done by Kapitza (8) and by Allen and Misener (9) using the capillary flow method, seemed to indicate that the viscosity of helium II was several orders of magnitude lower than that of helium I.

Other properties which indicate the inadequacy of a classical description for liquid helium were the so-called fountain effect and the existence of supersurface films. Both these properties seemed to indicate that the heat transfer and the mass transfer in helium II were inseparably interconnected (10).

The first to tackle the problem theoretically was F. London (11) who in 1938 advanced the hypothesis that the phenomenon of Bose-Einstein condensation, with due allowance made for the presence of interparticle interactions and for the liquid state of the substance, might be the essential cause of the  $\lambda$ -transition in liquid helium. This is made highly plausible





by the simple fact that whereas the heavier isotope of helium (namely  $\text{He}^4$ ) displays the phenomenon of  $\lambda$ -transition the lighter isotope (namely  $\text{He}^3$ ) does not. Moreover, the temperature at which the ideal Bose gas, with the same atomic mass and density as liquid  $\text{He}^4$ , undergoes Bose-Einstein condensation turns out to be about  $3.14^\circ\text{K}$ , which is of the very order of magnitude as the transition temperature in liquid helium. London went on to suggest that the superflow of  $\text{HeII}$  might be supposed to be connected especially with the condensed phase of the Bose gas. Further, there is some similarity (though not very much) in the temperature dependence of the specific heat in the two cases. Whereas liquid helium shows a logarithmic discontinuity in the specific heat at the transition point, the ideal Bose gas shows a discontinuity only in the derivative  $\left(\frac{\partial C_V}{\partial T}\right)_V$  of the specific heat. Of course, in the Bose gas model, the specific heat  $C_p$  does become infinite at the transition temperature. An important difference is met with in connection with the behaviour of  $C_V$  at low temperatures. While liquid helium shows a  $T^3$ -behaviour, the ideal Bose gas shows a  $T^{3/2}$  behaviour.

Despite these shortcomings, London's hypothesis did provide a theoretical basis for the two-fluid model of liquid helium, which had been suggested by Tisza (12) on purely empirical grounds. This model rested on the following major assumptions (13):



1) There exists in liquid helium II a superfluid component plus an excited normal fluid component. At  $T = 0^\circ\text{K}$ , the whole of the liquid is superfluid. As the temperature is raised excitations are created whose density increases monotonically with temperature; these excitations constitute the normal fluid. At  $T \geq T_\lambda$ , the whole of the liquid is in the normal state.

2) The viscosity and the entropy of the superfluid component are identically zero. The viscosity and the entropy of liquid helium II are, therefore, due to the normal component alone.

These assumptions at once remove the apparent discrepancy in the viscosity measurements. In the capillary flow experiments the normal component is completely held back and the flow is all due to the superfluid component. Consequently the measured viscosity is practically zero. In the oscillating disc experiments, however, the superfluid component remains unattached while the normal component becomes involved in the oscillatory motion. The measured coefficient of viscosity then depends on the fraction  $\rho_n/\rho$  of the normal component of the liquid.

The explanation for the existence of second sound in liquid helium also follows easily from these assumptions. If the temperature at some point in the fluid is suddenly raised, excitations will be created at that point leading to a non-uniformity in the density of the normal component. A resulting flow of normal fluid away from that point will occur with a corresponding flow of superfluid component towards it. Entropy



non-uniformities can thus be propagated as temperature waves through liquid helium II. This phenomenon was first studied by Tisza (12) in 1940 and Landau (14) in 1941.

Although experiments bore out many of the predictions of the two-fluid model, it remains primarily an intuitive model, not based on any rigorous theory except on the relevance of the Bose-Einstein condensation to the observed phenomena of superfluidity.

The two-fluid model was given a new life by Landau (14). In 1941, Landau suggested that the liquid helium be regarded as a quasi-continuum, whose low-lying excitations were quantized in the same manner as Debye modes in a solid. Landau assumed two kinds of elementary excitations: (i) phonons, which are the quanta of longitudinal sound waves, governed by the energy spectrum  $\epsilon = pc$ , where  $p$  is the momentum of the phonon and  $c$  is the velocity of sound in the liquid, and (ii) rotons, whose energy is assumed to be separated from the lowest state by an energy gap  $\Delta$ . Both types of excitations are supposed to have an effective mass and momentum which are ultimately attributed to the normal component of the liquid. The energy spectrum of the rotons may be written as

$$\epsilon = \Delta + \frac{(p - p_0)^2}{2\mu}, \quad (1.3)$$

where  $\Delta$ ,  $p_0$  and  $\mu$  are the parameters of the spectrum. The precise values of these parameters are hard to obtain but have been found by means of neutron scattering experiments (15); thus





we have

$$\Delta/k = 8.65^\circ\text{K}, p_0/\hbar = 1.91\text{\AA}^{-1}, \mu = 0.16m_{\text{He}}.$$

The existence of another kind of excitation has been proposed by Kuper (16); these are associated with the vibrational modes of the free surface of the liquid and are considered to be of the nature of "quantized capillary waves" or the so-called ripplons. The energy spectrum of these excitations is

$$\omega^2 = g k + \frac{\sigma k^3}{\rho}, \quad (1.4)$$

where the first term arises from the influence of gravity on the vibrations of the surface while the second term arises from the surface tension of the liquid. The concept of quantized surface modes of vibration has proved very useful in understanding the temperature variation of the surface tension of liquid helium and also leads to a significant contribution towards the zero-point surface tension of the liquid. Of course, the property of surface tension arises intrinsically from the interparticle interactions in the system. A study along these lines has been carried out in Chapters 2 and 3.

Other studies based on the two-fluid model of helium II that have been carried out here relate to the lambda temperature depression that occurs in helium films and is supposed to occur in rotating helium. These problems have been discussed in detail in Chapters 5 and 6.





A number of microscopic theories have also been developed in order to understand the physical behaviour of liquid helium from a more fundamental standpoint. Difficulties in developing a workable theory from first principles, however, stem from the fact that the substance under study is in the liquid state, which of all the states of matter is the least understood. Nevertheless, the theories of Bogolyubov(17) and Lee, Huang, and Yang (18) have succeeded in explaining some of the qualitative features of the liquid helium behaviour. These theories have, almost invariably, employed a hard-sphere interaction as a model potential between the helium atoms. However, in order to study liquid helium on a more realistic basis, especially in regard to properties that belong exclusively to the liquid state, one must not overlook the attractive part of the interaction. Without this part of the interaction, the system cannot even exist in the liquid state. The attraction may, of course, be too weak to cause two-body bound states in the medium, but it must at any rate be strong enough to form an N-body bound state. The N-body system will consequently possess an equilibrium density at which the total energy of the system is negative. Therefore, when attractive interactions of reasonable strength are present it is no longer necessary to fix the volume of the system by means of external boundaries. In fact, if the volume of the container is larger than that determined by the equilibrium density of the liquid, a free<sup>surface</sup>/appears. A study of the nature of this free surface



and a calculation of the free energy associated with it, on the basis of the imperfect-gas model of Gross and Pitaevski, constitutes the first major content of this thesis. By means of this approach, we obtain a theoretical estimate of the "intrinsic" surface tension of liquid helium; see Chapter 3.

We propose to review other, more particular, properties and concepts relating to liquid helium in the introductory sections of the relevant chapters of the thesis.



## TEMPERATURE DEPENDENCE OF THE SURFACE TENSION OF HELIUM II

## 2.1 INTRODUCTION

The surface tension of liquid helium was originally measured by van Urk, Keesom, and Kamerlingh Onnes (19) in 1925 and by Allen and Misener (20) in 1938. Extrapolating the results obtained at 0°K, they observed that, starting from a value of 0.35 erg cm<sup>-2</sup>, the surface tension at first decreases gradually but begins to decrease more rapidly as the critical point is approached. Recent experimental work by Atkins and Narahara (21) on the determination of the surface tension of helium<sup>4</sup> for temperatures down to 0.35°K has shown that the temperature dependence of the surface tension can be expressed by an empirical relationship of the form

$$\sigma(T) = \sigma(0) - aT^n ; \quad (2.1)$$

here,  $\sigma(0)$  is the limiting value of the surface tension as  $T \rightarrow 0^\circ\text{K}$ , while  $a$  and  $n$  are adjustable parameters. The best fit, using the method of least squares, was obtained with  $\sigma(0) = 0.3729 \text{ erg cm}^{-2}$ ,  $a = 0.0081 \text{ erg cm}^{-2} \text{ }^\circ\text{K}^{-n}$ , and  $n = 2.5 \pm 0.2$ . A complete theoretical understanding of the observed behaviour of  $\sigma(T)$ , as depicted by Eq. (2.1) was, however, still lacking.

The most satisfactory theory we have so far of the surface tension of liquid helium II is the one due to Atkins who, in an earlier paper (22), suggested that the major contribution to the surface energy of this liquid comes from the quantized surface modes of vibration known as ripplons. Atkins assumed these surface modes to be similar in nature to the macroscopic capillary waves which have a frequency-dependent phase velocity given by (23)





$$v = (2\pi\sigma v/\rho)^{1/3}, \quad (2.2)$$

where  $\sigma$  is the surface tension of the liquid,  $\rho$  is its density and  $v$  is the frequency of the wave. In the spirit of the Debye theory of solids, Atkins chose a cutoff frequency  $v_c$ , such that the total number of normal modes in the surface was equal to the total number of atoms in a monomolecular layer at the surface. This fixed the cutoff frequency at about  $10^{11}$  per second and the corresponding characteristic temperature  $\theta_c (= \hbar v_c/k)$  at a few degrees Kelvin.

Thus, according to Atkins' theory, a part of the observed surface tension  $\sigma(T)$  of liquid helium arises from the presence of quantized surface modes, which themselves arise due to the surface tension of the liquid. Accordingly, we must invoke an "intrinsic" surface tension,  $\sigma_i(T)$  say, of this liquid, with the result that the observed surface tension  $\sigma(T)$  can be expressed as

$$\sigma(T) = \sigma_i(T) + \sigma_v [T, \sigma_i(T)], \quad (2.3)$$

$\sigma_v$  being the contribution arising from the vibrational modes of the surface which would depend upon the temperature of the liquid explicitly as well as implicitly---the latter through the temperature dependence of  $\sigma_i(T)$  itself. Of course, it will be natural for us to look for the origin of  $\sigma_i(T)$  in the basic interactions among the atoms of the fluid. This problem will be pursued in Chapter 3.

In the limit of  $0^\circ\text{K}$ , Eq. (2.3) reduces to (22)

$$\sigma(0) = \sigma_i(0) + \frac{\hbar}{7\pi^{1/4}} \left( \frac{8\sigma_i(0)}{\rho^{1/3}\delta} \right)^{1/2}, \quad (2.4)$$





the second term on the right representing the zero-point contribution of the surface modes. In order to appreciate the relative magnitudes of the two terms in (2.4), we note that to obtain the experimental estimate of  $0.37 \text{ erg cm}^{-2}$  for  $\sigma(0)$ , we require  $\sigma_i(0)$  to be about  $0.14 \text{ erg cm}^{-2}$ , leaving about  $0.23 \text{ erg cm}^{-2}$  for  $\sigma_v(0)$ . The contribution of the surface modes is, therefore, more than appreciable!

At non-zero temperatures, especially for  $T \ll \theta_c$ , the added contribution of the surface modes (as arising from the explicit dependence on temperature) turns out to be (4)

$$-1.55 \left( \frac{\rho}{\sigma(0)} \right)^{2/3} \frac{k^{7/3}}{h^{4/3}} T^{7/3} = -6.5 \times 10^{-3} T^{7/3} \text{ erg cm}^{-2} . \quad (2.5)$$

The exponent  $7/3$  is quite consistent with the empirical value of  $2.5 \pm 0.2$ ; however, the numerical factor here is about 20% lower than the corresponding empirical value. It is, however, quite imaginable that the temperature dependence of  $\sigma_i(T)$  itself could, to some extent, account for the remainder.

An alternative explanation of the temperature dependence of the surface tension of liquid helium has been attempted by Singh (24), who adopted the ideal gas model for this liquid but made use of a better enumeration of the eigenfunctions in a bounded continuum, viz.

$$g(p) dp = \frac{4\pi V}{h^3} p^2 dp + \frac{\pi A}{2h^2} p dp + \dots, \quad (2.6)$$

where  $V$  is the volume of the enclosure, and  $A$  its surface area. The positive sign of the surface term is due to the fact that Neumann boundary conditions have been adopted, i.e.  $\frac{d\psi}{dn} = 0$  at



the surface. The above enumeration takes into account the so-called surface effects in the expression for the density of states. Singh thereby obtained for the temperature-dependent part of the surface tension the expression

$$\frac{-\pi m k^2 \zeta(2) T^2}{2h^2} = -7.5 \times 10^{-3} T^2 \text{ erg cm}^{-2}; \quad (2.7)$$

here,  $m$  is the mass of a helium atom, while the Riemann function  $\zeta(2)$  is equal to  $\pi^2/6$ . Comparing (2.7) with the empirical result of Atkins and Narahara, one finds that the numerical factor is now much closer to the corresponding empirical value, but that the exponent is significantly low. From the point of view of agreement with the experimental data, therefore, there is not much reason to choose one or the other of the two alternatives (2.5) and (2.7). From a physical point of view, however, we note that whereas the theoretical basis for (2.5) is sufficiently sound, the adequacy of using the ideal gas model for liquid helium, which led to (2.7) is hardly acceptable. Of course, Singh's argument does advocate a closer examination of the surface effects than has hitherto been done; however, in studying the contribution of these effects to the density of states and hence to the free energy of liquid helium, we must consider a gas of actual excitations, namely phonons and rotons, rather than one of non-interacting atoms. In the absence of interactions there would be no basis for expecting  $\sigma_1(0)$ , and hence  $\sigma(0)$  to be nonzero at  $T=0^\circ\text{K}$ .



In this chapter we shall settle the issue in regard to the surface effects that arise from a better enumeration of the density of states in a gas of excitations. In Sec. 2.2, we shall consider the thermodynamics of an  $n$ -dimensional ideal Bose gas of quasi-particles (excitations) taking into account "surface" effects that may be important. In Sec. 2.3 the surface energy contributions made by phonons and rotons are calculated and it will be shown that, regardless of boundary conditions chosen, these are negligible compared to the free energy contributions due to ripplons. The temperature dependence of the surface tension of helium II can thus be adequately explained by the existence of quantized surface modes of vibration.





## 2.2 THE n-DIMENSIONAL BOSE GAS

In order to study the physical properties of a statistical system a knowledge of the asymptotic distribution of single particle states, which are eigenfunctions of the Schrödinger equation

$$\nabla^2 \psi + \underline{k}^2 \psi = 0, \quad (\underline{k} = \underline{p}/\hbar) \quad (2.8)$$

is essential. Customarily, the number of eigenstates  $g(p)$  with momenta not exceeding a particular value  $p$  is approximated by the familiar Rayleigh-Weyl expression

$$g(p) = \frac{4\pi V}{3} (p/\hbar)^3, \quad (2.9)$$

where  $V$  is the volume of the enclosure. Of course, the validity of this expression rests on the assumption that the linear dimensions of the enclosure are much larger than the characteristic wavelength  $(\hbar/p)$ . A more rigorous study of the density of states, as allowed by (2.8) shows that the second term of the asymptotic expression for  $g(p)$ , of which (2.9) is the main term is directly proportional to the surface area  $S$  of the enclosure (25) (26). This surface term is naturally of a very direct physical interest to us for, when taken into account in calculating the extensive properties of a physical system, it leads to what might be called a "surface contribution" to the customary bulk values of these properties.

In order to appreciate the accuracy made possible by the inclusion of the surface term, Pathria (25) has tabulated a set



numbers adapted from an earlier work by Bolt (27), who computed the actual frequency distribution of acoustical eigentones (under the Neumann boundary condition) for a number of rooms of various sizes. In a typical case, when the room size was 10' by 15' by 30', the numerical value of  $g(v)$ , taking  $c=1125$  ft/sec, were as given in the last column of Table 2.1.

Table 2.1

Frequency $v$ (cps)	$g(v)$ , asymptotic		$g(v)$ actual (from Bolt)
	Volume term alone	Volume term and Surface term	
60	3	7	8
100	13	24	25
150	45	70	74
200	106	151	159
250	207	277	283
300	358	458	464

The second column of the table gives the numbers due to the volume term alone, while the third column takes into account the surface term as well. Clearly, the surface term makes a very important contribution to  $g(v)$ ; at the same time, the final remainder appears to be very small.

For the sake of complete generality, the enclosure that we



shall consider is an  $n$ -dimensional domain,  $D^{(n)}$  say. For such a domain Fedosov (26) has established the following asymptotic formula:

$$\int_0^K (K-k)^\xi dg(k) = \sum_{i=n}^1 a_i \frac{\xi! i!}{(\xi+i)!} K^{\xi+i} + o(K^{n-1}), \quad (2.10)$$

so that, with  $\xi = 0$ , one obtains

$$g(K) = \sum_{i=n}^1 a_i K^i + o(K^{n-1}). \quad (2.11)$$

The coefficients  $a_i$  here are related to certain geometrical measures of the domain, viz.

$$a_n = \frac{\text{mes}_n D^{(n)}}{2^n \pi^{n/2} \left(\frac{n}{2}\right)!}, \quad (2.12)$$

and

$$a_{n-1} = \frac{\sum_j \text{mes}_{(n-1)} S_j^{(n-1)}}{2^{n+1} \pi^{(n-1)/2} \left(\frac{n-1}{2}\right)!}, \quad (2.13)$$

where  $S_j^{(t)}$  is a  $t$ -dimensional "face" of the domain; the upper sign corresponds to the Dirichlet boundary condition  $\psi = 0$ , and the lower sign corresponds to the Neumann boundary condition  $\frac{d\psi}{dn} = 0$ .

For a three-dimensional domain of arbitrary shape, Eq. (2.12)



and (2.13) yield the formula

$$g(K) = \frac{K^3}{6\pi^2} V - \frac{K^2}{16\pi} S + o(K^2) \quad (2.11')$$

Now, the error term as such rather appears to vitiate the role of the surface term in the expression for  $g(K)$ . However, Pathria (25) has provided sufficient computational evidence (see Table 2.1) to show that the error term in (2.11') is in effect much inferior to the surface term, so that Eq. (2.11') may be replaced by

$$g(K) = \frac{K^3}{6\pi^2} V - \frac{K^2}{16\pi} S + o(K^2). \quad (2.11'')$$

Using (2.12) and (2.13) we can calculate the thermodynamic functions of an  $n$ -dimensional Bose gas. We have, quite generally,

$$\frac{PV}{kT} = - \sum_{\underline{p}} \ln (1 - z e^{-\beta \epsilon_{\underline{p}}}). \quad (2.14)$$

The summation can be converted into an integral employing the expression (2.11), along with (2.12) and (2.13), for the density of states. Again, for the sake of generality, we take the energy-momentum relationship for the quasi-particles to be  $E = \alpha p^S$ . We then obtain





$$PV \equiv k T \ln \mathcal{Z} = \frac{\pi^{n/2} \left(\frac{n}{s}\right)! g_{\left(\frac{n}{s}+1\right)}(z) V_n}{\left(\frac{n}{2}\right)! h^n \alpha^{n/s}} (kT)^{\frac{n}{s}+1}$$

$$+ \frac{\pi^{\frac{n-1}{2}} \left(\frac{n-1}{s}\right)! g_{\left(\frac{n-1}{s}+1\right)}(z) A_n}{4 \left(\frac{n-1}{2}\right)! h^{n-1} \alpha^{\frac{n-1}{s}}} (kT)^{\frac{n-1}{s}+1}, \quad (2.15)$$

where  $g_n(z) = \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^n}$ .

The internal energy can be found from Eq. (2.14) yielding the result

$$U = \frac{\left(\frac{n}{s}\right) \pi^{n/2} \left(\frac{n}{s}\right)! g_{\frac{n}{s}+1}(z) V_n}{\left(\frac{n}{2}\right)! h^n \alpha^{n/s}} (kT)^{\frac{n}{s}+1} \quad (2.16)$$

$$+ \frac{\left(\frac{n-1}{s}\right) \pi^{\frac{n-1}{2}} \left(\frac{n-1}{s}\right)! g_{\frac{n-1}{s}+1}(z) A_n}{4 \left(\frac{n-1}{2}\right)! h^{n-1} \alpha^{\frac{n-1}{s}}} (kT)^{\frac{n-1}{s}+1}$$

The number of particles in the excited states can also be found with the result



$$N_e = \frac{\pi^{n/2} \left(\frac{n}{s}\right)! g_{\frac{n}{s}}(z) V_n}{\left(\frac{n}{2}\right)! h^n \alpha^{n/s}} (kT)^{n/s}$$

$$+ \frac{\pi^{\frac{n-1}{2}} \left(\frac{n-1}{s}\right)! g_{\frac{n-1}{s}}(z) A_n}{4 \left(\frac{n-1}{2}\right)! h^{n-1} \alpha^{\frac{n-1}{s}}} (kT)^{\frac{n-1}{s}} \quad (2.17)$$

From the last relation it is easy to show in general the conditions necessary for Bose-Einstein condensation to occur in an infinite n-dimensional Bose gas. In fact, true Bose-Einstein condensation can occur only if the expression for the total number of excited particles (2.17) is bounded. Then if the total number of particles is greater than the maximum number of particles the excited states can hold, i.e. if

$$N > \frac{\pi^{n/2} \left(\frac{n}{s}\right)! \zeta\left(\frac{n}{s}\right) V_n (kT)^{n/s}}{\left(\frac{n}{2}\right)! h^n \alpha^{n/s}}$$

then the ground state of the system will be occupied. The transition temperature  $T_c$  is then defined as

$$T_c = \left\{ \frac{\left(\frac{n}{2}\right)! h^n \alpha^{n/s}}{\pi^{n/2} k^{n/s} \zeta\left(\frac{n}{s}\right) \left(\frac{n}{s}\right)!} \frac{N}{V_n} \right\}^{s/n} \quad (2.18)$$



A non-zero transition temperature is possible if and only if the Riemann zeta function  $\zeta(\frac{n}{s})$  remains bounded. This is true only if  $n > s$ . Hence for an infinite three dimensional Bose gas, since  $n = 3$  and  $s = 2$ , a true Bose-Einstein condensation temperature does exist. In the case of an infinite two-dimensional Bose gas Bose-Einstein condensation does not occur since  $\zeta(1)$  is unbounded and hence all the particles can be accommodated in the excited states. Peculiarly enough, for an extreme relativistic, infinite two-dimensional Bose gas, since  $\epsilon = pc$  (where  $c$  is the speed of light) true Bose-Einstein condensation does occur since now  $n = 2$ ,  $s = 1$  and  $\zeta(2)$  is bounded.

Now, since  $F = \mu N - PV$ , where  $\mu$  is the chemical potential of the Bose gas, then below the transition temperature (where  $\mu = 0$ ) we have  $F = -PV$ . Considering only the surface term of (2.15), we have, in the case of ideal-gas particles ( $n = 3$ ,  $\alpha = \frac{1}{2}m$ ,  $s = 2$ ),

$$F_s/A = \pm \frac{\pi m \zeta(2)}{2h^2} (kT)^2 = \pm 7.5 \times 10^{-3} T^2 \text{ erg cm}^{-2}, \quad (2.19)$$

which is exactly the result obtained by Singh. Eq. (2.19) can also be derived without making use of the explicit expression for  $g(K)$ . In that case, one works with the summations as such by applying the theta-function transformation to the sums; for the details see Appendix I. Still another way of deriving this result is through the construction of the Mellin transforms of the relevant summands and evaluating the resulting complex contour integrals (28). For the phonons ( $n = 3$ ,  $\alpha = c$  (the speed of sound),  $s = 1$ ) one obtains





$$F_s/A = \pm \frac{\pi \zeta(3)}{2h^2 c^2} (kT)^3 = \pm 1.96 \times 10^{-4} T^3 \text{ erg cm}^{-2}, \quad (2.20)$$

This result can also be derived by the use of Mellin transforms (28).

For rotons it is necessary to make a separate calculation because their energy-momentum relationship does not fall into the category  $E = \alpha p^s$ . One has, in this case,  $E = \Delta + \frac{(p-p_0)^2}{2\mu}$ . A straight-forward calculation making use of formulae (2.11') gives

$$\begin{aligned} F_s/A &\approx \pm kT \frac{\pi}{2h^2} \int_{-\infty}^{\infty} e^{-\left[\Delta + \frac{(p-p_0)^2}{2\mu}\right]/kT} p \, dp \\ &= \pm \frac{(2\pi^3 \mu)^{1/2}}{2h^2} p_0 e^{-\Delta/kT} (kT)^{3/2} \\ &= \pm 3.1 \times 10^{-2} e^{-\Delta/kT} T^{3/2} \text{ erg cm}^{-2} . \end{aligned}$$



### 2.3 SURFACE FREE ENERGY OF RIPPLONS

Before applying the thermodynamics of Section (2.2) to calculate the surface free energy of the ripples we shall have to derive the necessary energy-momentum relation for surface waves.

The basic equations required in order to derive the dispersion relation for hydrodynamic capillary waves are (i) Laplace's equation (29)

$$p - p_0 = - \sigma \left( \frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right), \quad (2.22)$$

where  $\zeta$  is the normal displacement of the surface, and (ii) Euler's equation for an incompressible, irrotational fluid in a gravitational field

$$\frac{\partial \underline{v}}{\partial t} + \frac{1}{2} \text{grad } v^2 = - \text{grad} \left( \frac{P}{\rho} + gz \right) \quad (2.23)$$

In this case we have potential flow and can write  $\underline{v} = \text{grad } \phi$ , so that  $\phi$  is the velocity potential. Equation (2.23) then reads

$$\text{grad} \left( \frac{\partial \phi}{\partial t} + \frac{1}{2} v^2 + P/\rho + gz \right) = 0,$$

and hence, choosing the arbitrary function  $\underline{p}(t)$  to be zero,

$$p = - \rho gz - \rho \frac{\partial \phi}{\partial t} - \frac{1}{2} \rho v^2. \quad (2.24)$$

Considering only small velocities of the fluid, and



neglecting the term  $\frac{1}{2} \rho v^2$ , we substitute Eq. (2.21) into Eq. (2.22) and obtain the relation

$$\rho g z + \rho \frac{\partial \phi'}{\partial t} - \sigma \left( \frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right) = 0. \quad (2.25)$$

Here we have redefined the potential  $\phi' = \phi + (P_0/\rho)t$ ; this makes no essential difference since  $\underline{v} = \text{grad } \phi = \text{grad } \phi'$ .

We can differentiate this relation with respect to  $t$  and replace  $\frac{d\zeta}{dt}$  by  $\frac{\partial \phi}{\partial z}$ , obtaining

$$\rho g \frac{\partial \phi}{\partial z} + \rho \frac{\partial^2 \phi}{\partial t^2} - \sigma \frac{\partial}{\partial z} \left( \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) = 0. \quad (2.26)$$

Assuming now a plane wave propagating in the  $x$ -direction, say  $\phi = A e^{kz} \cos(kx - \omega t)$  and substituting into (2.26) we obtain the dispersion relation

$$\omega^2 = gk + \frac{\sigma k^3}{\rho}. \quad (2.27)$$

For long wavelengths, such that  $k \ll \sqrt{g\rho/\sigma}$ , we have pure gravity waves. In the opposite case of short wavelengths we have capillary waves, or ripplons

$$\omega^2 = \frac{\sigma k^3}{\rho} \quad (2.28)$$

We can now use Equation (2.15) to calculate the free energy of these excitations and consequently the contribution to the surface tension of helium II below the transition point.



For ripplons, the energy-momentum relationship, when the effect of the gravitational field can be neglected, is

$$E = \left(\frac{\sigma}{\rho h}\right)^{1/2} p^{3/2}, \quad (2.29)$$

so that we have  $\alpha = \left(\frac{\sigma}{\rho h}\right)^{1/2}$ ,  $s = 3/2$ . Since ripplons constitute a surface phenomenon (rather than a correction to some bulk value), the desired result in this case follows from the main term in (2.15) with  $n = 2$  and  $V_2 = A$ . One thus obtains

$$\begin{aligned} F/A &= -\pi \left(\frac{\rho}{2\pi\sigma}\right)^{2/3} h \left(\frac{kT}{h}\right)^{7/3} \Gamma\left(\frac{7}{3}\right) \zeta\left(\frac{7}{3}\right) \\ &= -6.5 \times 10^{-3} T^{7/3} \text{ erg cm}^{-2}. \end{aligned} \quad (2.30)$$

This is precisely the result obtained earlier by Atkins (22).

A comparison of (2.20) with (2.30) readily shows that the surface effect of the phonon component is hardly a few percent of the direct contribution of the ripplons. The surface effect of the roton component, as given by (2.21), is still less by a factor of 10 or more. Moreover, a basic difficulty with the surface effects (2.20) and (2.21) is that they are so strongly dependent on the nature of the boundary conditions used. Thus, we see that the observed temperature dependence of the surface tension of liquid helium is, in the main, given by the direct surface energy of the quantized waves on the surface of the liquid.





## CHAPTER 3

### INTRINSIC SURFACE TENSION OF HELIUM II AT $T=0^\circ\text{K}$

#### 3.1 INTRODUCTION

In this chapter we attempt to explain the existence of the limiting surface tension  $\sigma(o)$  on the basis of the atomic interactions. The theoretical model employed for this investigation consists of a dilute, imperfect gas of bosons, interacting through a two-body potential  $V(\underline{r}-\underline{r}')$  which can be replaced by a pseudopotential  $V_0\delta(\underline{r}-\underline{r}')$  where  $V_0$  is a constant that depends upon the strength of the interaction. It is well known that this model has been successfully employed by Gross (31) and by Pitaevski (32) to demonstrate the possibility of existence of quantized vortex motion in a Bose fluid and to investigate inhomogeneous states of a Bose system. We employ this model to investigate the nature of the inhomogeneity at the free surface of a Bose liquid and compute thereby the energy associated with a unit area of the surface. This leads quite naturally to a nonvanishing value of the intrinsic surface tension  $\sigma_i(o)$ , whence follows the vibrational part of the surface tension,  $\sigma_v(o)$ , so that finally we have an estimate for the observed surface tension at  $T=0^\circ\text{K}$ . The resulting theoretical estimate of  $0.28 \text{ erg cm}^{-2}$  compares favourably with the experimental estimate of  $0.37 \text{ erg cm}^{-2}$  (3,43).



### 3.2 THE IMPERFECT GAS MODEL

As a model, we consider the case of particles interacting by means of weak, two-body forces, taking the self-consistent field theory as the first approximation (33). We shall assume that the range of the interparticle force is much greater than the average interparticle spacing, so that the rapidly changing forces on a particle are less important than the smoothly varying average force. Under these assumptions one can start the analysis with the Hartree approximation.

We assume the ground state wave function to be a product of single-particle wavefunctions.

$$\Psi(\underline{x}_1, \dots, \underline{x}_N; t) = \prod_{i=1}^N g(\underline{x}_i, t)$$

$$\int |g(\underline{x}, t)|^2 d^3x = 1, \quad (3.1)$$

where  $g(\underline{x}_i, t)$  is a normalized single-particle state. We also assume that  $g(\underline{x}_i, t)$  is separable such that

$$g(\underline{x}, t) = g(\underline{x}) \exp \left[ -i\mu t/\hbar \right].$$

The single-particle wave function  $g(\underline{x}, t)$  is thus an approximate stationary state of the hamiltonian

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} V(\underline{x}_i - \underline{x}_j). \quad (3.2)$$

If we renormalize the wavefunction  $g(\underline{x})$  and let  $\psi(\underline{x}) = \sqrt{N} g(\underline{x})$ , we then have  $\int |\psi(\underline{x})|^2 d^3x = N$  and  $|\psi(\underline{x})|^2$  will represent



the density of the fluid. In terms of  $\psi(\underline{x})$  the time-dependent self-consistent field equation becomes

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + \psi(\underline{x}) \int |\psi(\underline{y})|^2 V(\underline{x}-\underline{y}) d^3y. \quad (3.3)$$

The energy of a stationary state is

$$E = \frac{\hbar^2}{2m} \int |\nabla \psi(\underline{x})|^2 d^3x + \frac{1}{2} \int |\psi(\underline{x})|^2 V(\underline{x}-\underline{y}) |\psi(\underline{y})|^2 d^3x d^3y. \quad (3.4)$$

The complex wave function  $\psi(\underline{x},t)$  thus governs the behavior of the superfluid condensate.

The analysis can be much simplified if we replace  $V(\underline{x}-\underline{y})$  by the approximate pseudo-potential  $V_0 \delta(\underline{x}-\underline{y})$ , where (34)

$$V_0 = \left( \frac{4\pi a \hbar^2}{m} \right)^{1/2}.$$

This does not alter the general nature of the results for phenomena whose characteristic length - the thermal wavelength,  $\lambda = h/2\pi mkT)^{1/2}$  - is larger than the range of the force. The simpler equation is then

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + \frac{4\pi a \hbar^2}{m} |\psi|^2 \right\} \psi = \mu \psi, \quad (3.5)$$

where we see that  $\mu$ , the chemical potential, is just the energy increase in the system when one more particle is added to it.

Depending upon the boundary conditions used, solutions of the equations of the type (3.5) can often be found in terms of elliptic functions. Abrikosov (35) has discussed approximate





solutions of this equation in relation to type II superconductors. In the case of the noninteracting Bose gas contained in a box of macroscopic dimensions with rigid walls the solution possesses the absurd feature of exhibiting an enormous density near the center of the container. Solutions of Eq.(3.5) have the virtue of giving an almost uniform density distribution in the system, except near the rigid walls of the box, or near the vortex cores. Ginzburg and Pitaevski (36) have used a similar equation in order to discuss the lambda temperature shift in liquid helium films. In many cases it is useful to apply certain integral relations, discussed by Schiff (37), Derrick (38) and by Darewych and Schiff (39), which can considerably simplify integrals of the type (3.4).



### 3.3 SURFACE NON-UNIFORMITY AND FREE ENERGY

We shall apply Eq. (3.5) to study only the surface part of the fluid, for it is in this part alone that we have a variation of  $n(\underline{r})$  from the bulk value to a vanishingly small value, over a region characterized by some sort of a "healing length". It is, however, important to note that the existence of a free surface, which is one of the basic characteristics of a liquid, as opposed to a gas, necessarily requires that the atoms in the surface region of the liquid experience, consequent upon a small outward displacement, a predominantly attractive force toward the interior of the fluid; consequently, the effective scattering length of interaction for the atoms in this so-called surface layer must be negative (40), i.e.  $a = -|a|$ .

Now, considering a free surface normal to the x-axis, so that the operator  $\nabla^2$  in (3.5) is just  $d^2/dx^2$ , and denoting the value of  $n(x)$  at the point of inflexion (see Fig 3.1) by  $n_s$ , we obtain for the parameter  $\mu$ ,

$$\mu = \frac{4\pi a \hbar^2}{m} n_s \quad . \quad (3.6)$$

The differential equation (3.5) can then be written as

$$\frac{d^2\psi}{dx^2} + 8\pi|a|\psi^3 = 8\pi|a|n_s\psi \quad (3.7)$$

Introducing the reduced variables

$$\psi_o(x) = \psi(x)/n_s^{1/2}; \quad \xi = x/\ell, \quad (3.8)$$



where  $\ell = (8\pi n_s |a|)^{-1/2}$ , the differential equation becomes

$$\frac{d^2\psi_0}{d\xi^2} + \psi_0^3 - \psi_0 = 0. \quad (3.9)$$

The relevant solution of this equation that we shall consider is the one that vanishes at  $\xi \rightarrow \infty$ , and has a vanishing slope at, say  $\xi = 0$ . This corresponds to a density varying from a bulk value  $n(0)$  at  $x=0$  to a vanishingly small value over the distance of a healing length  $\ell$ . For all  $\xi < 0$ , i.e. everywhere in the bulk of the liquid, we shall take  $n(x) = n(0) = n_0$ .

We find as a solution

$$\psi_0 = \sqrt{2} \operatorname{sech} \xi, \quad (3.10)$$

and, accordingly, for the superfluid density

$$n(x) = 2n_s \operatorname{sech}^2 \left( \frac{x}{\ell} \right). \quad (3.11)$$

As  $x \rightarrow 0$ , the particle density approaches the value  $2n_s$ , which should be equal to the bulk value  $n_0$ . Thus, the point of inflexion of the  $(\psi_0, \xi)$  curve (see Fig 2.1) corresponds to a particle density exactly one-half of the bulk value, which is clearly a very satisfactory situation. In terms of the bulk density  $n_0$  the solution is thus

$$n(x) = n_0 \operatorname{sech}^2 \left( \frac{x}{\ell} \right). \quad (3.12)$$

This density variation is similar to that found by Cahn and Hilliard (40) in the case of a classical fluid. Cahn and



Hilliard minimized the free energy in a region of non-uniform composition near the critical temperature and obtained the density variation

$$n(x) = \frac{n_0}{2} \left[ \tanh\left(\frac{x}{\ell}\right) + 1 \right], \quad (3.13)$$

where  $\ell \propto (T - T_c)^{-1/2}$ . The authors also calculate the corresponding interfacial free energy to be proportional to  $(T_c - T)^{3/2}$ .

Considering again Fig. 2.1, the dashed line in the graph indicates the spatial region which would be occupied by the particles now constituting the non-uniform surface layer if they were spread out uniformly with a density equal to  $n_0$ . Thus  $\ell = (4\pi|a|n_0)^{1/2}$  is a measure of the extent of the spatial inhomogeneity in the free surface; in magnitude, it is comparable to the lateral dimension of the "core" of the quantized vortex!

The structural energy per unit area associated with the non-uniformity in the free surface can be determined by calculating the difference between the energy per unit area of the surface layer as it is and that of the corresponding layer if the distribution were uniform. One thereby has

$$\begin{aligned} \frac{F - F_0}{A} &= \frac{E - E_0}{A} = \frac{\hbar^2}{2m} \int_0^\infty \left( \frac{d\psi}{dx} \right)^2 dx + \frac{2\pi|a|\hbar^2}{m} \left[ \int_0^\infty |\psi(x)|^4 dx \right. \\ &\quad \left. - \int_0^\ell n_0^2 dx \right] = \frac{1}{3} \frac{\hbar^2 n_0}{m\ell} = \frac{2\pi^{1/2}\hbar^{1/2}}{3m} n_0^{3/2} |a|^{1/2}. \quad (3.14) \end{aligned}$$

It is difficult to find a theoretical estimate for the scattering





length  $a$ . However, Girardeau (41) has discussed the imperfect Bose gas under the influence of an attractive interaction and has arrived at an estimate for  $a \approx -2\text{\AA}$ . If we use this value, we obtain for the surface tension of helium II,

$$\sigma_i(o) = 0.09 \text{ erg cm}^{-2} \quad (3.15)$$

The existence of the intrinsic surface tension would lead to the presence of ripplons on the free surface which, in turn, would give rise to a zero-point free energy. Atkins (4) has carried out this calculation earlier with the result

$$\begin{aligned} \sigma_v(o) &= \int_0^c \left( \frac{1}{2} h v \right) g(v) dv \\ &= \frac{h}{7\pi^{1/4}} \left( \frac{8\sigma_i(o)}{\rho \delta^2} \right)^{1/2}, \end{aligned} \quad (3.16)$$

which, on substitution from (3.14) becomes

$$\sigma_v(o) = \frac{8\pi}{7\sqrt{3}} \frac{h^2}{m} \frac{n_o^{1/4} |a|^{1/4}}{\delta^{1/2}}. \quad (3.17)$$

Substituting the relevant values in this expression we obtain

$$\sigma_v(o) = 0.19 \text{ erg cm}^{-2}. \quad (3.18)$$

Combining  $\sigma_i(o)$  and  $\sigma_v(o)$ , we obtain for the observed surface tension  $\sigma(o)$  of  $\text{He}^4$  an estimate of  $0.28 \text{ erg cm}^{-2}$ ; the corresponding experimental estimate is  $0.37 \text{ erg cm}^{-2}$ .

Of course, on the basis of a gaseous model, though interacting, we cannot expect to understand the behaviour of a liquid



quantitatively, especially when the numerical value used for the scattering length is not very reliable. In fact, if we took a value for the scattering length  $a = -4\text{\AA}$ , the agreement with experiment would be excellent. Qualitatively, in any case, the theory developed here indeed appears to be a step in the right direction.

Finally, we remark that, since the temperature dependence of the surface tension of liquid helium is very well explained up to approximately  $1.5^\circ\text{K}$  by the surface energy contribution of the surface waves, the intrinsic surface tension  $\sigma_i$  may not be expected to be strongly temperature-dependent near  $T=0^\circ\text{K}$ . One also expects this from consideration of the third law of thermodynamics. Since the entropy  $S = - \left( \frac{\partial F}{\partial T} \right)_\mu$ , we can write the surface part of the entropy as

$$S_s = - \frac{\partial F_s}{\partial T} = - s \frac{\partial \sigma}{\partial T},$$

where  $s$  is the surface area of the system and  $\sigma$  its surface tension. Thus, since the entropy is zero at  $T=0^\circ\text{K}$ , clearly  $\frac{\partial \sigma}{\partial T} = 0$  at  $T=0^\circ\text{K}$ .



### 3.4 SURFACE TENSION OF HELIUM<sup>3</sup>

Since helium<sup>3</sup> is a Fermi liquid, while helium<sup>4</sup> is a Bose liquid, the difference in statistics would seem to imply that no one theory could satisfactorily explain certain phenomena occurring in both liquids. However, if statistical effects were unimportant for certain phenomena, for example, the surface tension of the liquid, then, perhaps one theory could give adequate results for both liquids. In fact, if statistical effects are neglected, the theory developed above can, quite successfully, be applied to liquid He<sup>3</sup>.

We will show that the surface tension of liquid He<sup>3</sup> can be understood along similar lines as that of He<sup>4</sup>, although we cannot, of course, claim a strong theoretical basis for this treatment. We shall use as our basic equation Eq.(3.5), but cannot speak in terms of ground-state wave functions, but will use Eq.(3.5) as differential equation for the density distribution of the fluid and calculate the free-energy associated with the density non-uniformity at the surface.

Since the zero-point energy of the atoms plays an important part in determining the surface energy of a liquid at low temperatures, liquid He<sup>3</sup> would be expected to have a surface tension much smaller than that of liquid He<sup>4</sup>. In fact, the surface tension of He<sup>3</sup> at  $T=0^\circ\text{K}$  can be extrapolated to a value of  $0.153 \text{ erg cm}^{-2}$ .

Lovejoy(42) has found that the assumption concerning the existence of surface waves also explains reasonably well the





temperature dependence of the surface tension of  $\text{He}^3$  up to approximately  $1.5^\circ\text{K}$ . He also had to invoke an intrinsic surface tension in order to support the quantized wave motion. This intrinsic surface tension can also be reasonably well explained by the theory of Section 3.2. We shall adopt a similar approach as used by Amit and Gross (43), in considering Eq.(3.5) not as a wave equation, but as an equation to determine the distribution of fluid density over the surface region. Thus we rewrite Eq. (3.5)

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + \frac{4\pi a \hbar^2}{m} n(x) \right\} \sqrt{n(\underline{x})} = \mu \sqrt{n(\underline{x})} \quad , \quad (3.19)$$

where  $\mu$  is a parameter which can again be determined at the point of inflexion of the Curve (3.1) and we have

$$\mu = (2\pi |a| \hbar^2 / m) n_0 \quad .$$

From this equation, we obtain as a solution just Eq.(3.11)

$$n(x) = n_0 \operatorname{sech}^2 \left( \frac{x}{\ell} \right) .$$

We also rewrite the equation for the energy due to the surface non-uniformity in terms of the density

$$\frac{E-E_0}{A} = \frac{\hbar^2}{2m} \int \left[ \nabla \sqrt{n(\underline{x})} \right]^2 d^3x + \frac{2\pi |a| \hbar^2}{m} \int \left[ n(x) - n(0) \right]^2 d^3x . \quad (3.20)$$

Now since the boiling point, critical point, and density of  $\text{He}^3$  are appreciably less than the corresponding values for



He<sup>4</sup> (see Table 3.1), the molecules of He<sup>3</sup> are farther apart than the molecules of He<sup>4</sup>. Consequently, the attractive interaction, while still present in the surface region, is much smaller in He<sup>3</sup> than in He<sup>4</sup>. The scattering length then, while still negative, should be considerably smaller in magnitude. If we take a value for  $a \approx -1\text{\AA}$  we obtain  $\sigma_i(o) = 0.04 \text{ erg cm}^{-2}$  and  $\sigma_v(o) = 0.11 \text{ erg cm}^{-2}$ . We can thus obtain good agreement with experiment up to approximately 1.5°K.

Table 3.1 (44) Some Equilibrium Properties of Liquid Helium-3 and Helium-4: Normal Boiling Point (N.B.P); Critical Temperature,  $T_c$ ; Critical Density  $\rho_c$ ; Density  $\rho_o$  at 0°K.

	N.B.P.	$T_c$	$\rho_c$	$\rho_o$
He <sup>3</sup>	<b>3.19</b>	3.33	0.0413	0.082
He <sup>4</sup>	4.21	5.21	0.0675	0.146

Atkins (4) and Lovejoy (42) have suggested that the reason why the surface tension of He<sup>4</sup> and He<sup>3</sup> depart from theoretical predictions at approximately 1.5°K is that the simple two-dimensional Debye model does not take into account sufficiently



the higher frequency surface waves. Secondly, at higher temperatures, the wavelengths of the surface waves become comparable to the interatomic distance so that the energy-momentum relationship for ripplons will be affected. A third reason is, of course, that as the critical temperature is approached, the intrinsic surface tension itself begins to decrease rapidly, to disappear at  $T_c$ . It is probable that the temperature dependence of the intrinsic surface tension is thus responsible for the departure of the experimental results from the theoretical predictions around 1.5°K.



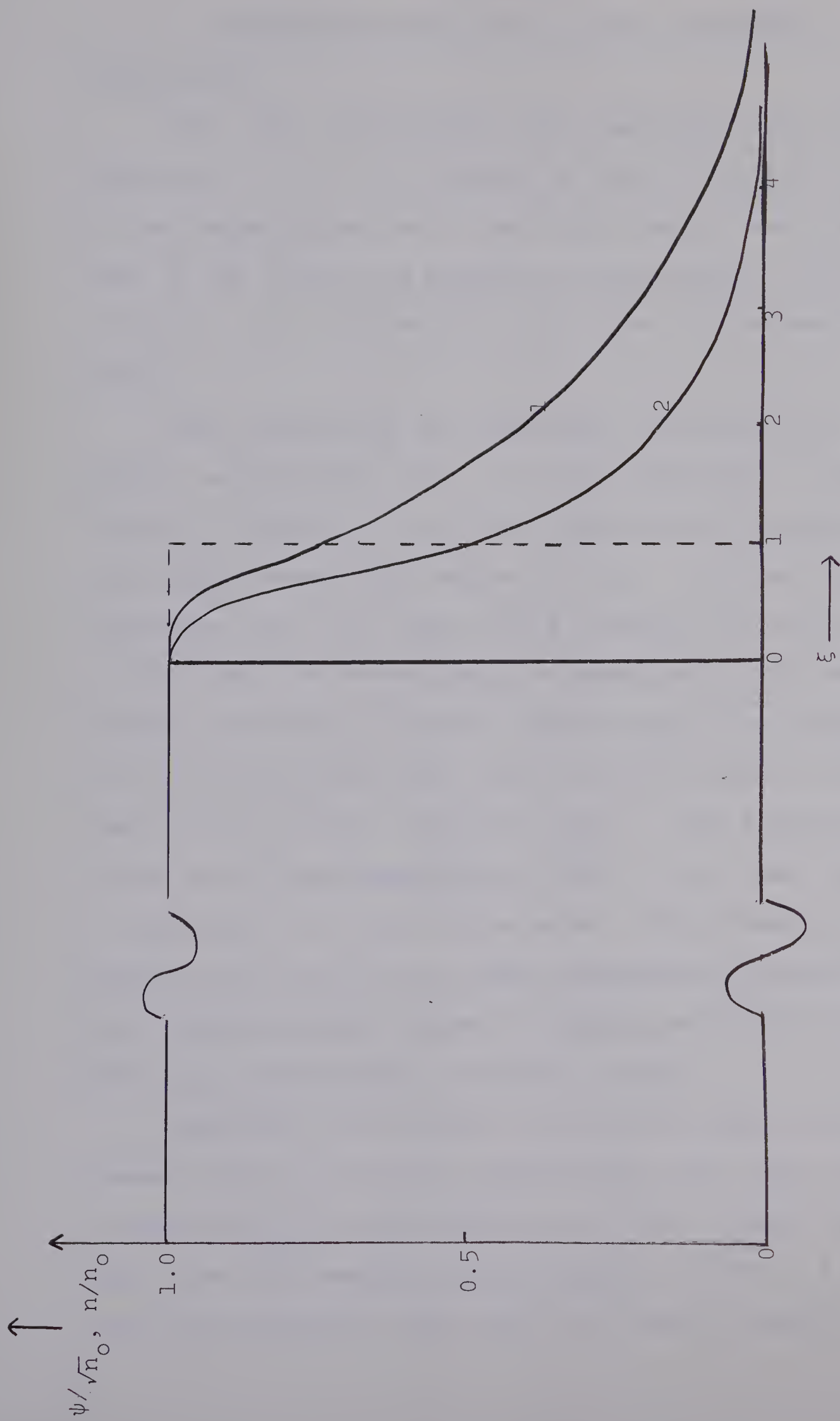


Fig. 3.1 Variation of the superfluid wave function (curve 1) and of the superfluid density (curve 2) at the free surface. The dashed line indicates the spatial extent of the fluid if the density were uniform throughout.





## CHAPTER 4

### SURFACE TENSION AT THE $\text{He}^3$ - $\text{He}^4$ INTERFACE

#### INTRODUCTION

Since 1946, when Franck (46) suggested that a phase separation of the two isotopes  $\text{He}^3$  and  $\text{He}^4$  might be expected at low temperatures due to the fact that  $\text{He}^3$  would not take part in the superfluid phenomena characteristic of liquid helium II, much research has been done on mixtures of  $\text{He}^3$  and  $\text{He}^4$ .

Phase separation was discovered experimentally by Walters and Fairbank (47). As the temperature of the  $\text{He}^3$ - $\text{He}^4$  mixture is lowered, a critical temperature is reached at which phase separation begins to occur. As the temperature approaches zero, the upper phase becomes very nearly pure, the  $\text{He}^4$  fraction decreasingly exponentially with temperature. However, contrary to initial expectations, the concentration of  $\text{He}^3$  in the lower phase does not go to zero as the temperature of the mixture approaches zero. This finite solubility of  $\text{He}^3$  in  $\text{He}^4$  was suggested in 1961 by van Leuwen and Cohen (48) on the basis of a hard sphere model. Measurements by Edwards et al (49) of the phase separation curve by means of a heat capacity method showed a limiting solubility of  $\text{He}^3$  in  $\text{He}^4$  in the lower phase of 6% at  $T = 0^\circ\text{K}$ .

Liquid  $\text{He}^3$ - $\text{He}^4$  systems also exhibit superfluidity. However, down to very low temperatures,  $\text{He}^3$  does not partake in superfluid flow, but forms part of the normal fluid. In fact, when the temperature is suddenly raised in a region of the liquid mixture, there will be a flow of normal fluid and



$\text{He}^3$  away from this region and a corresponding flow of superfluid toward it. Consequently, the equilibrium distribution of  $\text{He}^3$  in the mixture is very sensitive to small heat currents, a fact which strongly affected initial experimental results on  $\text{He}^3$ - $\text{He}^4$  mixtures.

In 1949, Abraham, Weinstock, and Osborne (50) discovered that the  $\lambda$ -temperature depended upon the concentration of  $\text{He}^3$  in  $\text{He}^4$ . This was contrary to expectations based on the classical ideal solutions, which would have a  $\lambda$ -point independent of concentration. It was found, however, that the  $\lambda$ -temperature decreased almost linearly with the concentration of  $\text{He}^3$  in  $\text{He}^4$ . The simplest theoretical derivation of the  $\lambda$ -temperature in  $\text{He}^3$ - $\text{He}^4$  mixtures was advanced by Heer and Daunt (51) in 1951. They treated the  $\text{He}^4$  component as an ideal gas, quite independent of the presence of  $\text{He}^3$ , and the transition temperature of this ideal gas is

$$T_{\lambda} = \frac{h^2}{2\pi m_4} \left( \frac{N_4}{2.612 V_m} \right)^{2/3}, \quad (4.1)$$

where  $V_m = N_3 v_3 + N_4 v_4$ ,  $v_3$  and  $v_4$  being the mean volumes per atom in pure liquid  $\text{He}^3$  and  $\text{He}^4$  respectively. The change in the  $\lambda$ -temperature is therefore a consequence in the change in  $V_m/N_4$  and hence

$$\frac{T_{\lambda}(x_3)}{T_{\lambda_0}} = \left[ \frac{1 - x_3}{1 + x_3 \left( \frac{v_3}{v_4} - 1 \right)} \right]^{2/3}, \quad (4.2)$$



where  $x_3$  is the mole fraction of  $\text{He}^3$  in the mixture. This theory predicts the initial slope of the  $T_\lambda$  versus  $x_3$  curve to be -1.9, whereas experimentally the slope ( $\partial T_\lambda / \partial x_3$ ) of the curve is approximately -1.5 (52).

Another property of liquid  $\text{He}^3$ - $\text{He}^4$  mixtures that depends upon the relative concentration of the two components is the surface tension. The surface tension of the mixture can be expressed approximately in terms of the surface tensions of the pure liquids, i.e.

$$\sigma = x \sigma_3 + (1-x) \sigma_4 + \sigma_e , \quad (4.3)$$

where  $\sigma_e$  is a small positive "excess" surface tension (53).

In this chapter, however, we shall be concerned with a discussion of the interfacial surface tension of a liquid  $\text{He}^3$ - $\text{He}^4$  system at  $T = 0^\circ\text{K}$ , i.e., after phase separation has occurred. The predicted value for the interfacial tension depends critically upon the model one adopts for the surface tension of a quantum liquid. In Section 4.2 we will calculate the value of the interfacial surface tension as predicted by the "classical" theory of surface tension, which has been applied by Amit and Gross to liquid  $\text{He}^4$ , and in Section 4.3 we will calculate the value of the interfacial tension as predicted by Atkins' model.





## 4.2 CLASSICAL INTERFACIAL SURFACE TENSION

In the "classical" theory of the surface tension of a liquid, the zero point energy of the surface modes of vibration plays no part. This is, no doubt, correct in the case of classical liquids in which case the zero point energy of surface modes of vibration is only an infinitesimal part of the total value of the surface energy. However, Amit and Gross (54) have used the classical theory to calculate the surface tension of liquid He<sup>4</sup> and obtain reasonable experimental argument. The authors assumed a trial density pattern for the liquid

$$\begin{aligned} \rho(x) &= 4\rho_0 a^2 \frac{x^2}{(x^2+a^2)} , & x \leq a \\ \rho(x) &= \rho_0 , & x \geq a \end{aligned} \quad (4.4)$$

where  $x$  is the perpendicular distance from the wall and  $a$  is a parameter to be determined by minimizing the surface energy obtained. The energy can be expressed as an integral by using Eq. (3.4).

$$\begin{aligned} E/S &= \frac{\hbar^2}{2m} \int_0^a \left( \frac{d\sqrt{\rho}}{dx} \right)^2 dx + \frac{\bar{V}}{2} \int_0^a \left[ \rho(x)^2 - \rho_0^2 \right] dx \\ &+ \bar{V} \rho_0 \int_0^a \left[ \rho_0 - \rho(x) \right] dx , \end{aligned} \quad (4.5)$$

where  $\bar{V} = \int V(r) d^3r$ . Using (4.4) and performing the integral one arrives at:

$$E/S = m\rho_0 \left[ 0.73 \frac{\hbar^2}{m^2 a} + 0.16 c^2 a \right] . \quad (4.6)$$



When this is minimized with respect to  $a$  one obtains

$$E/S = 0.7 \hbar c \rho \approx 0.4 \text{ erg cm}^{-2}, \quad (4.7)$$

which agrees reasonably well with experiment.

In order to obtain an estimate of the interfacial surface tension of a liquid  $\text{He}^3$ - $\text{He}^4$  system, based on the classical model, we shall apply Antonoff's rule (55) to calculate the interfacial tension  $\sigma_{34}(0)$  at  $T = 0^\circ\text{K}$ ,

$$\sigma_{34}(0) \approx \sigma_4(0) - \sigma_3(0), \quad (4.8)$$

$\sigma_4(0)$  being the equilibrium surface tension between liquid  $\text{He}^4$  and its vapour at  $T = 0^\circ\text{K}$  and  $\sigma_3(0)$  the equilibrium surface tension between liquid  $\text{He}^3$  and its vapour at  $T = 0^\circ\text{K}$ . In a number of experiments on a phase-separated phenol-water system, Antonoff et al (56) found that the measured interfacial tension agreed to within experimental error with the prediction from Antonoff's rule. Of course, we must first correct  $\sigma_4(0)$  for the fact that, on phase-separation at  $T = 0^\circ\text{K}$ , the lower phase may still contain a 6% admixture of  $\text{He}^3$ . Hence, using Eq. (4.3), neglecting the small excess surface tension  $\sigma_e$  we obtain the result

$$\sigma_{34}(0) \approx 0.36 - 0.15 = 0.21 \text{ erg cm}^{-2}. \quad (4.9)$$

On the other hand, if the "quantum" theory of the surface tension of a quantum liquid is correct, then the interfacial



surface tension  $\sigma_{34}(0)$  must be regarded as made up of two contributions, i.e.

$$\sigma_{34}(0) = \sigma_{34i}(0) + \sigma_{34v}(0) \quad , \quad (4.10)$$

where, as usual,  $\sigma_{34i}(0)$  is the intrinsic interfacial tension and  $\sigma_{34v}(0)$  is the contribution made by the capillary waves at the interface. Clearly enough, it is then only  $\sigma_{34i}(0)$  which can be obtained by applying the Antonoff rule; and again taking into account the 6% concentration of  $\text{He}^3$  in  $\text{He}^4$  at  $T = 0^\circ\text{K}$ , we obtain

$$\begin{aligned} \sigma_{34i}(0) &\approx \sigma_{4i}(0) - \sigma_{3i}(0) \\ &\approx 0.134 - 0.04 \approx 0.094 \text{ erg cm}^{-2}. \end{aligned} \quad (4.11)$$

The contribution  $\sigma_{34v}$  must be calculated separately from the zero point energy of the capillary waves at the interface.



### (4.3) VIBRATIONAL MODES AT THE INTERFACE

Consider a liquid of density  $\rho'$  and depth  $h'$  flowing with constant velocity  $V'$  over a liquid of density  $\rho$  and depth  $h$  which flows with constant velocity  $V$ .

We take the  $x$ -axis in the interface separating the fluids, with  $y$  being measured vertically upward from the interface at equilibrium. It can be shown (57) that the complex potential for the lower fluid is just

$$w = - (V-c)z - \frac{a(V-c)}{\sinh m h} \cos m (z + i h), \quad (4.12)$$

where  $c$  is the speed of propagation of the surface waves,  $m = 2\pi/\lambda$ , and  $a$  is a constant. The streamline  $\Psi = 0$  then becomes  $\eta = a \sin m x$ , where  $\eta$  is the vertical displacement of the interface from equilibrium. The complex potential for the upper fluid can be obtained by writing,  $V', -h'$ , for  $V, h$ . The speed in the lower liquid is then given by

$$q^2 = \frac{dw}{dz} \frac{d\bar{w}}{d\bar{z}} = (V-c)^2 - \frac{2ma(V-c)^2}{\sinh m h} \cosh m (y+h) \sin m x,$$

and the speed at the interface ( $y=0$ ) is then

$$q_0^2 = (V-c)^2 \left[ 1 - 2m \eta \coth m h \right], \quad (4.13a)$$

and, for the upper liquid,

$$q_0'^2 = (V'-c)^2 \left\{ 1 + 2m \eta \coth m h' \right\}. \quad (4.13b)$$





Bernoulli's equation for the two liquids just gives

$$p' + \frac{1}{2} \rho' q_0'^2 + \rho' g \eta = \text{const.} \quad (4.14a)$$

$$p + \frac{1}{2} \rho q_0^2 + \rho g \eta = \text{const.} \quad (4.14b)$$

However, in the presence of an interfacial surface tension  $\sigma$  we have the relation

$$p' - p = \sigma/R = -\sigma \frac{d^2\eta}{dx^2} = \sigma m^2 \eta. \quad (4.15)$$

Hence subtracting (4.14b) from (4.14a) and using (4.15) we have

$$\frac{1}{2} \rho' q_0'^2 - \frac{1}{2} \rho q_0^2 + g \eta (\rho' - \rho) - \sigma m^2 \eta = \text{const.} \quad (4.16)$$

Now, substituting  $q_0'^2$  and  $q_0^2$  from (4.13) and setting the coefficient of  $\eta$  equal to zero (since the r.h.s. of (4.16) is constant) we obtain

$$\begin{aligned} & m \rho (V-c)^2 \coth m h + m \rho' (V'-c)^2 \coth m h' \\ & = g(\rho - \rho') + \sigma m^2. \end{aligned} \quad (4.17)$$

Letting  $h = -h' = \infty$  for our situation, we obtain the result

$$c^2 = \frac{\lambda g}{2\pi} \frac{\rho - \rho'}{\rho + \rho'} + \frac{2\pi\sigma}{\lambda(\rho + \rho')}. \quad (4.18)$$

As usual, we shall consider only short wavelength vibrations so that the effect of gravity can be neglected. The cutoff frequency  $\gamma_c$  can be determined in the same way as for a pure liquid. It is essentially the difference in the number of particles per unit area in the adjacent layers on opposite sides of the



interface that are responsible for the restoring force when a small displacement of the surface is made (assuming that the interparticle interaction is essentially the same for both fluids). Hence the cutoff frequency  $\nu_c$  of these modes is determined by requiring that their total number per unit area of the interface be equal to the difference between the number of molecules per unit area of the high density phase on the one hand and the low density phase on the other. It turns out that  $\nu_c \approx 4.3 \times 10^{10} \text{ sec}^{-1}$  for the interfacial modes which may be compared with the values  $9.5 \times 10^{10} \text{ sec}^{-1}$  for liquid  $\text{He}^3$  and  $1.5 \times 10^{11} \text{ sec}^{-1}$  for liquid  $\text{He}^4$ . Carrying out the relevant calculation for the zero-point energy of the interfacial waves, in the same way as was done in Section (3. ), we obtain

$$\sigma_{34v}(0) \approx 0.007 \text{ erg cm}^{-2} \quad , \quad (4.19)$$

which is extremely small in comparison with the intrinsic surface tension (4.11). Consequently, the theoretical estimate for the  $\text{He}^3\text{-He}^4$  interfacial tension would be

$$\sigma_{34}(0) \approx 0.10 \text{ erg cm}^{-2} \quad , \quad (4.20)$$

which is about one-half of the classical estimate. An extrapolation of experimental determinations of the  $\text{He}^3\text{-He}^4$  interfacial tension should therefore be able to decide the issue between the two estimates and provide a practical justification for expressing the surface tension of a quantum liquid as a sum of two contributions of a different nature.



## CHAPTER 5

### LAMBDA TEMPERATURE DEPRESSION IN HELIUM FILMS

#### 5.1 INTRODUCTION

Although film flow had been observed much earlier, the existence of a helium film in equilibrium covering a vertical surface in contact with a helium II bath was first postulated by Rollin (61) in 1936, to explain the anomalous character of the heat flow in the liquid. The existence and properties of such a film were first clearly elucidated in a series of experiments performed by Daunt and Mendelssohn (62) in 1939.

Some of the more important of their results were:

- 1) Helium II creeps in the form of a film over all solid surfaces in contact with the bath level, as long as the temperature of these surfaces is well below the  $\lambda$  point.
- 2) The transfer of the film is nearly frictionless and the rate of transfer is in the first approximation, independent of the pressure head, or the length of the path to be traversed.
- 3) The superfluid flows up a temperature gradient. Such a film flow is thus an example of "ideal" superfluidity since no corresponding normal fluid flow occurs in this manner.
- 4) Saturated helium II films (in equilibrium with the saturated vapor) achieve a thickness of approximately  $300 \text{ \AA}$  at a height of 1 cm. above the surface of the bulk liquid.

Unsaturated films - films in equilibrium with a gas at a pressure  $p$  less than the saturated pressure  $p_0$  - have also been







studied. However, as pointed out by Rice and Widom (63), there is a possible connection between saturated and unsaturated films. If we imagine a saturated film at a height  $H$  above the bath in equilibrium with the saturated vapour, then the pressure at large distances from the wall is

$$p = p_0 \exp \left( -\frac{mgH}{RT} \right)$$

Hence an unsaturated film at a relative pressure  $p/p_0$  can be regarded as having identical properties as a saturated film in equilibrium with the saturated vapour at a height  $H$  above the bulk liquid given by

$$H = \frac{RT}{mg} \ln (p/p_0).$$

Hence, when we discuss helium II films in this chapter, we shall not differentiate between saturated and unsaturated films.

Since at low temperatures the helium atom is chemically inert the formation of the film is clearly an example of physical rather than chemical adsorption. The force necessary for holding the film to the wall must be the van der Waals attraction between the helium atoms and the wall.

Another important property of helium II films is that the  $\lambda$ -temperature in such films may be considerably depressed below the bulk value, and the magnitude of this depression depends upon the film thickness.

Frederikse (64) in 1949 noticed that in helium II films, the specific heat maximum becomes smeared out and occurs at lower temperatures than the bulk specific heat maximum. It also appeared at this time that, for a given film thickness, the onset temperature for superflow was well below that of the



specific heat maximum. Later experiments (65) showed that in very fine channels of diameter approximately  $70\text{\AA}$ , the two temperatures were the same. It has been concluded experimentally by Brewer et al (66) that the disparity between the specific heat maximum and the onset temperature for superflow in thin films is consistent with the presence of excitations associated with the free surface of the helium II film. As these excitations could not be present in filled fine pores, the two temperatures would be expected to agree. These authors conclude that for a given film thickness, superfluidity dies out at a well-defined temperature above which, however, the excitations contributing to the specific heat still remain until the ordered phase is completely destroyed. The experimental curves for the temperature at which the specific heat maximum occurs can be fitted near the bulk  $\lambda$ -point as

$$\Delta T = \frac{0.24 \times 10^{-14}}{(t - 3.2 \times 10^{-8})^2} \text{ } ^\circ\text{K}.$$

The temperature for the onset of superfluidity obeys approximately the empirical relation

$$\Delta T = \frac{0.92 \times 10^{-14}}{(t - 3.2 \times 10^{-8})^2} \text{ } ^\circ\text{K}.$$

Here, the first layer of helium II near the wall is considered to be solid. However, there is at present no agreement on this point (67); hence we shall not make this assumption in our calculations.

In this chapter we shall attempt to explain theoretically the depression of the  $\lambda$ -temperature on the basis of the existence of excitations at the free surface and in the region of non-uniform density near the wall. In section 5.2 we shall outline



the attempts based on the ideal Bose-Einstein gas theory to explain the  $T_\lambda$  depression. In Section 5.3 we review the Ginzburg-Pitaevski theory which is based on an analogy with the corresponding Landau-Ginzburg theory of superconductivity. In Section 5.4, we discuss several modifications of the Ginzburg-Pitaevski theory, and in the subsequent section we present our own theoretical calculations.





## 5.2 FINITE THREE-DIMENSIONAL BOSE-EINSTEIN SYSTEMS

Since the  $\lambda$ -transition occurs only in  $\text{He}^4$  and not in  $\text{He}^3$ , it appears that statistical correlations must play a fundamental role in accounting for the  $\lambda$ -transition and for many other superfluid properties of  $\text{He}^4$ . There are many reasons, however, why Bose-Einstein condensation cannot account even qualitatively for the behaviour of  $\text{He}^4$  near the  $\lambda$ -transition. Although Bose-Einstein condensation of the ideal gas takes place at a temperature comparable to the  $\lambda$ -temperature, the thermodynamic behaviour of the ideal gas near the transition temperature is very different from that of  $\text{He}^4$ . For example, whereas experimentally one observes a logarithmic singularity in the specific heat at the  $\lambda$ -point, the Bose-Einstein gas predicts a maximum in the form of a cusp. Moreover, whereas the ideal gas predicts a  $C_V \propto T^{3/2}$  behaviour near  $T=0^\circ\text{K}$ , the experimentally observed temperature dependence of the specific heat is just that due to phonons, namely  $C_V \propto T^3$ . These discrepancies are certainly not surprising since the theory of the ideal Bose-Einstein gas does not take into account atomic interactions. It is clear that one has to take into account not only the effect of the short-range repulsive forces in  $\text{He}^4$ , but also the weak attractive forces which are responsible for the liquefaction of  $\text{He}^4$  at low temperatures.

A number of attempts have also been made to explain the depression of the  $\lambda$ -temperature in thin helium films on the basis of the ideal-gas model. Osborne (68) showed in 1949 that although the two-dimensional Bose-Einstein gas does not





undergo true condensation, it is possible to define an accumulation temperature at which a rapid accumulation of particles into the ground state occurs. This accumulation temperature is non-zero for a finite two-dimensional system, but tends to zero as the size of the system is increased without limit, as we have already shown in Section 2.2.

It was also shown by Ziman (69) that a finite three-dimensional ideal Bose-Einstein system behaves in many ways like the two-dimensional system. One can similarly define an accumulation temperature, which is non-zero when the dimensions of the system are of comparable length, but goes to zero when any two of the dimensions are increased without limit. The perfect gas theory thus predicts that the  $\lambda$ -temperature should depend on the size and the shape of the container in a definite way: for a given thickness of the helium film, the lambda temperature should go to zero as the two lateral dimensions are made much larger than the thickness of the film. This is, of course, in complete disagreement with experimental observations.

In 1953, Ziman (69) suggested an ideal-gas model, with the aim of reconciling the discrepancies between the experimental results and the predictions of the ideal gas. Ziman suggested that the model to be adopted for liquid helium was made up of a very large number of finite, ideal Bose-Einstein cells whose size is determined by some characteristic length of  $\text{He}^4$ . These cells were to have in common the same temperature and the same chemical potential but were to be otherwise completely independent. Then for those films that have a thickness less



than the size of the characteristic cells or assemblies, finite size effects should be observed. The characteristic extent of these assemblies were chosen by Ziman in such a way that one obtains the best numerical correspondence between the variations with film thickness of the predicted accumulation temperature and the actual temperature.

Ziman's model predicted a satisfactory value for the thickness of a saturated film below the  $\lambda$ -point and also suggested a possible explanation of the magnitude of the characteristic velocity of flow through superleaks. However, the model does not make satisfactory predictions of the thermodynamic behaviour about liquid helium in the neighbourhood of the  $\lambda$ -point, neither in thin films nor in bulk samples.

Goble and Trainor (70) have improved upon the numerical results obtained by Ziman. By means of extensive computer calculations, they evaluated the thermodynamic quantities pertaining to Ziman's model by carrying out explicitly the summations involved rather than replacing them by integrations, as is customarily done. They also discussed the condensation process in finite systems and showed that small Bose-Einstein assemblies retain important features characteristic of the condensation process. However, they noted that a suggestion by Khorana and Douglass (71), namely that the procedure used by London (72) for determining the condensation point in bulk systems was to be used for finite systems also, is misleading. Goble and Trainor point out that there is no unique procedure for defining the condensation temperature in finite systems.





In fact, the authors considered six different criteria for evaluating the transition temperature in a finite assembly of size  $L \times L \times D$ , where  $D \ll L$  (corresponding to a thin film). All the six criteria can be used in the case of bulk systems also, in which case one obtains the same transition temperature. However, for thin films, different criteria lead to different results.

For completeness and for possible later reference, we reproduce in Table 5.1 the numerical results obtained by Goble and Trainor. The different transition temperatures have the following meanings:

1.  $T_c$  corresponds to the maximum value of  $\left[ \frac{\partial^2 (N/N_0)}{\partial T^2} \right]$ ,
2.  $T_{cp}$  corresponds to the minimum value of  $\left[ \frac{\partial^2 \mu}{\partial T^2} \right]$ ,
3.  $T_L$  is obtained by setting  $E_0 - \mu = 0$  in the expression for the total number of particles,
4.  $T_m$  is the temperature at which the maximum occupation of the first excited state occurs,
5.  $T_e$  is obtained by extrapolating the  $N_0/N$  vs.  $T$  curve,
6.  $T_1$  is the temperature at which the specific heat attains its maximum.

The experimental results for helium films, which are given in the last column were obtained by Long and Meyer (73). The temperature values have been renormalized in order to bring the various condensation temperatures for bulk samples into agreement with the observed  $\lambda$ -temperature of  $2.18^\circ \text{K}$  in liquid helium.





Thickness D in Å	$T_c$	Renormalized Temperatures in °K					Experimental Value of $T_\lambda$
		$T_{cp}$	$T_2$	$T_m$	$T_e$	$T_1$	
0	0.65	0.52	-	0.49	0.54	$\infty$	-
10	1.36	1.17	0.94	1.13	1.30	3.24	1.46
25	1.98	1.79	-	1.80	1.91	-	1.83
60	2.17	2.09	2.03	2.01	2.14	2.38	2.14
750	2.18	2.18	2.18	2.18	2.18	2.18	2.18
Bulk	2.18	2.18	2.18	2.18	2.18	2.18	2.18

The transition temperature versus film thickness results in the first five columns are in qualitative agreement with the experimental results. However, whereas experimentally one observes that the specific heat maxima become less prominent and shift towards lower temperatures as the film thickness is reduced, Ziman's model predicts a shift of the specific heat maxima towards higher temperatures as the film thickness is decreased. As the authors point out, this is a defect shared by all ideal gas models. It appears therefore that a correct explanation of the  $\lambda$ -transition in thin films cannot be based on the ideal gas model but needs to take into account the atomic interactions. Moreover, it is possible that finite size effects alone, as considered by Goble and Trainor, may not be sufficient to explain the  $\lambda$ -temperature depression but that surface effects, as well as effects due to the van der Waals interaction between the helium atoms and the wall have to be taken into account.



### 5.3 GINZBURG-PITAEVSKI THEORY

In order to explain the phenomena of superconductivity and superfluidity, a number of macroscopic theories which do not begin with the elemental particles of the system, but with some gross, overall features of the whole system, have been developed. One such approach was developed by Landau (74) in 1937. The central idea of that approach was to expand the Gibbs free energy of the system in terms of a certain order parameter  $\psi$  about the transition temperature. In order for this approach to be valid, one considers only the region in which the order parameter is small, i.e., the region near the transition temperature:  $|T - T_c| \ll T_c$ .

In 1950 Landau and Ginzburg (75) applied the theory to the superconducting phase transition with great success. Eight years later, Ginzburg and Pitaevski applied the same theory to the superfluid transition, though not with the same measure of success.

In this section we review the Ginzburg-Pitaevski theory and its application to the depression of the lambda temperature in helium films. In Section 5.3 we shall consider some useful modifications of this theory.

The first assumption made in the theory is that the order function  $\psi(r)$  corresponds to an effective wave function of the superfluid component. Since  $\psi(r)$  is assumed to be a complex wave function, we can write

$$\psi(r) = \chi(r) e^{i\phi(r)} \quad (5.1)$$

The real functions  $\chi(r)$  and  $\phi(r)$  defined by (5.1) correspond to



the superfluid mass density  $\rho_s(r)$  and the superfluid velocity  $v_s(r)$  by the relations

$$\begin{aligned}\rho_s(r) &= m \chi^2(r), \\ v_s(r) &= \frac{\hbar}{m} \nabla \phi(r).\end{aligned}\tag{5.2}$$

Another assumption made in this theory concerns the functional form of the Gibbs free energy  $g(\psi)$ . Considering a system in which the normal component is at rest and is at a temperature close to the  $\lambda$ -temperature, we can expand  $g(\psi)$  in powers of the parameter  $\psi(r)$ , which, of necessity, is very small.

The functional form for  $g(\psi)$  that Ginzburg and Pitaevski take is the following:

$$g(\psi) = g_1 - \alpha |\psi|^2 + \beta/2 |\psi|^4 - \frac{\hbar^2}{2m} |\nabla \psi|^2.\tag{5.3}$$

Here the term  $g_1$  is the Gibbs free energy for the normal component; the next two terms are the free energy contributions of the superfluid component, and the last term represents the kinetic energy contribution from the superfluid component.

We then minimize  $g(\psi)$  with respect to  $\psi$  in order to determine  $\psi(r)$  from the resulting Euler equation which we can write as

$$-\frac{\hbar^2}{2m} \nabla^2 \psi - \alpha \psi + \beta |\psi|^2 \psi = 0.\tag{5.4}$$

This is the Ginzburg-Pitaevski equation which has the same form as Equation (3.5) although the coefficients have completely different meanings.

The third assumption concerns the pressure and temperature dependence of the parameters  $\alpha(P,T)$  and  $\beta(P,T)$ . Since the





transition is characterized by the solution  $\psi=0$  above and  $\psi \neq 0$  below, the parameter  $\alpha(P,T)$  must vanish at the transition. Also, for  $g(\psi)$  to be a minimum at the transition point, the coefficient  $\beta(P,T)$  of the fourth order term must be positive at the transition. The transition line is therefore characterized by the equation  $\alpha(P,T)=0$  (76).

Considering the transition for a given value of the pressure, Ginzburg and Pitaevski assume (after Landau (74))

$$\alpha(T) = \alpha'(T-T_\lambda) = -\alpha' \Delta T. \quad (5.5)$$

The coefficient  $\beta(T)$  is simply put equal to the constant  $\beta(T_\lambda)$ .

There is no reason why this expansion of the parameters  $\alpha(T)$  and  $\beta(T)$  should be valid. In fact, we shall see in Sec. (5.4) that the above expansion leads to an incorrect temperature dependence of the superfluid density.

The Ginzburg-Pitaevski theory can be applied to the problem of the transition temperature depression in  $\text{He}^4$  films. One first simplifies Equations (5.3) and (5.4) by introducing the dimensionless parameters

$$\begin{aligned} \psi_0 &= \psi/\psi_e & \psi_e &= \left(\frac{\alpha}{\beta}\right)^{1/2} \\ \xi_i &= x_i/\ell & \ell &= \hbar/(2m\alpha)^{1/2} \end{aligned} \quad (5.6)$$

The Gibbs free energy then takes the form

$$g(\psi) = g_1 - \frac{\alpha^2}{2} \left[ 2|\psi_0|^2 - |\psi_0|^4 - 2|\nabla_\xi \psi_0|^2 \right], \quad (5.7)$$

and the corresponding Euler equation becomes

$$\nabla_\xi^2 \psi_0 = [\psi_0^2 - 1] \psi_0 \quad (5.8)$$

For a film of thickness  $L$  in the  $z$ -direction, say, and infinite in extent in the  $x$  and  $y$  directions, Ginzburg and





Pitaevski took the boundary conditions corresponding to an impenetrable wall, i.e.,

$$\psi_0(\xi) = 0 \text{ for } \xi=0 \text{ and } \xi=L/\ell, \quad (5.9)$$

These boundary conditions are, strictly speaking, valid only for a film enclosed on both sides by impenetrable walls. The solution of Equation (5.8) with the boundary conditions (5.9) can be expressed in terms of an elliptic integral of the first kind (77)

$$\xi = \sqrt{2} \int_0^{\psi_0} \frac{dt}{\sqrt{t^4 - 2t + c}}, \quad (5.10)$$

which can be solved explicitly in terms of Jacobian elliptic functions. One obtains

$$\psi_0(\xi) = \frac{\sqrt{2-k}}{\sqrt{1+k^2}} \operatorname{sn}\left(\frac{\xi}{\sqrt{1+k^2}}; k\right) \quad (5.11)$$

where the modulus  $k$  is given by

$$\frac{L}{\ell} = 2\sqrt{1+k^2} K(k), \quad (5.12)$$

$K(k)$  being the complete elliptic integral of the first kind.

The constant  $C$  is expressed in terms of  $k$  as

$$C = \frac{4k^2}{(1+k^2)^2}$$

A plot of the function  $\psi$  has the form of a dome, which is symmetric with respect to the middle of the film and the height of which decreases with decreasing film thickness. Also, there is a film thickness below which no solution with  $\psi \neq 0$  exists, i.e. the film ceases to be superfluid. The order parameter  $\psi_0(\xi)$  can be seen from Eq. (5.11) to vanish when  $k=0$ , and hence we obtain from Eq. (5.12)

$$\frac{L}{\ell} = 2K(0) = \pi, \quad (5.13)$$



which defines a film transition temperature  $T_{\lambda}$  that differs from the bulk transition temperature by the amount

$$\Delta T_{\lambda} = \frac{-\pi^2 \hbar^2}{2m \alpha'} \cdot \left( \frac{1}{L^2} \right) . \quad (5.14)$$

The constants  $\alpha'$  and  $\beta$  can be evaluated from specific heat data. When these values are substituted into Eq. (5.14) one obtains

$$\Delta T_{\lambda} = \frac{2 \times 10^{-14}}{L^2} . \quad (5.15)$$

One finds that this result differs from the experimental values by about a factor of 3.



#### 5.4 MODIFICATIONS OF THE GINZBURG-PITAEVSKI THEORY

The Ginzburg-Pitaevski theory possesses a number of obvious shortcomings. First of all, as has been mentioned in the previous section, there is no basic reason why the expansion  $\alpha(T) = \alpha' (T - T_\lambda)$  should be valid. In fact, this expansion can be shown to lead immediately to an incorrect temperature dependence for the superfluid density:

$$\rho_s = m |\psi|^2 = \frac{m\alpha}{\beta} = \frac{m\alpha'}{\beta} (T - T_\lambda), \quad (5.16)$$

which disagrees with the experimentally well-established relation  $\rho_s \propto (T_\lambda - T)^{2/3}$  near the  $\lambda$ -transition (37,38).

Secondly, the Ginzburg-Pitaevski theory predicts a second-order phase transition in a bulk system. The Gibbs free energy in the bulk limit can be written from Eq. (5.3), using the relation  $\alpha(T) = \alpha' (T - T_\lambda)$ ,

$$g = g_1 - \frac{\alpha'^2}{2\beta} (T - T_\lambda)^2. \quad (5.17)$$

This clearly represents a second-order phase transition in contrast to the logarithmic behaviour of  $C_p$  near the lambda point.

Thirdly, the Ginzburg-Pitaevski theory predicts a second-order phase transition in films also (80). Measurements of  $C_p$ , however, show a very smooth behaviour at the superfluid transition temperature indicating thereby a higher order transition (81,82).

There are a number of obvious ways of "improving" the Ginzburg-Pitaevski theory to obtain better agreement with experiment. One can, for example, easily incorporate the logarithmic behaviour of  $C_p$  near  $T_\lambda$  into the theory by keeping the same functional form for  $g(\psi)$  but changing the temperature





dependence of the coefficients  $\alpha$  and  $\beta$  (80,83). According to such a scheme one chooses  $\alpha = -\alpha' \Delta T \beta(T)$ ,  $\beta(T) = \beta' \ln(-\Delta T)$ , so

$$\begin{aligned} \text{i)} \quad & |\psi|^2 = -\alpha' \Delta T, \\ \text{ii)} \quad & g = g_1 - \frac{1}{2} \alpha'^2 \beta' (\Delta T)^2 \ln(-\Delta T). \end{aligned} \quad (5.18)$$

Consequently one obtains the proper logarithmic behaviour for  $C_p$  near  $T_\lambda$ . However, the theory not only predicts a linear dependence of superfluid mass density on temperature, but when applied to the helium film shows no shift at all in the transition temperature.

Alternatively, one can choose the temperature dependence of  $\alpha$  and  $\beta$  so as to obtain the correct relationship between the superfluid density and the temperature. This was done by Mamaladze (84) in 1966. Mamaladze assumed that

$$\alpha = +\alpha' (T_\lambda - T)^{4/3}, \quad \beta = \beta' (T_\lambda - T)^{2/3}, \quad (5.19)$$

where  $\alpha$  and  $\beta$  are both positive. Substituting these parameters into Eq. (5.16), we readily obtain

$$\rho_s = \frac{m\alpha'}{2\beta'} (T_\lambda - T)^{2/3}. \quad (5.20)$$

We thus obtain the proper dependence of superfluid density on temperature. However, on substituting the parameters  $\alpha$  and  $\beta$  into the expression (5.3) for  $g(\psi)$  we obtain the Gibbs free energy

$$g(\psi) = g_1 - \frac{\alpha^2}{2\beta} = g_1 - \frac{1}{2} \frac{\alpha'^2}{\beta'} (T_\lambda - T)^2,$$

which again implies a second-order phase transition at the  $\lambda$ -temperature.

Modification of the temperature dependence of the parameters  $\alpha$  and  $\beta$  also leads to a new formula for the  $\lambda$ -temperature shift in films. Substituting Eq. (5.19) into Eq. (5.13) we obtain



$$\Delta T_{\lambda} = \frac{-2.5 \times 10^{-11}}{L^{3/2}}. \quad (5.21)$$

This does indeed give a better agreement with the experimental results near the lambda point. However, as has been pointed out by Wong (80) and Mamaladze (84) there is as yet no sound theoretical basis for the definition or redefinition of the parameters.

Amit (85,86) has further modified Mamaladze's theory. He noticed that, whereas the requirement that  $\psi=0$  give a stable minimum for  $g(\psi)$  at  $T=T_{\lambda}$ , is fulfilled by the original Ginzburg-Pitaevski theory since  $\beta$ , the coefficient of the  $|\psi|^4$  term was positive, this requirement is obviously not fulfilled by Mamaladze's theory since both the coefficients vanish at  $T=T_{\lambda}$ . To insure stability therefore one has to add a term of the form  $\gamma|\psi|^6$  where  $\gamma>0$ . We then have

$$g|\psi| = g_1 + (A + \frac{1}{2} m v_s^2) \psi^2 + B\psi^4 + C\psi^6, \quad (5.22)$$

where  $A = -\alpha(T_{\lambda}-T)^{4/3}$ ,  $B = \beta(T_{\lambda}-T)^{2/3}$ , as before. Using this theory Amit finds for the critical velocity  $v_c$  in a film

$$v_c = (2\alpha/m) (T_{\lambda}-T)^{2/3}, \quad (5.23)$$

and for the superfluid mass density

$$\rho_s(v_s=0) \propto (T_{\lambda}-T)^{2/3}. \quad (5.24)$$

Wong (80) has proposed the following modification of the Ginzburg-Pitaevski theory: he considers an order function  $\psi$ , to be defined later, and constructs the functional  $g(\psi)$  as

$$g(\psi) = g_1 + A|\psi|^2 + B|\psi|^3 + C|\psi|^4 + \frac{\hbar^2}{2m} |\nabla\psi|^2. \quad (5.25)$$

We now have two equations to define the lambda point

$$\begin{aligned} A(P_{\lambda}, T_{\lambda}) &= 0 \\ B(P_{\lambda}, T_{\lambda}) &= 0. \end{aligned} \quad (5.26)$$



By varying  $g(\psi)$  with respect to  $\psi$ , we now obtain a somewhat different Euler equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + A\psi + \frac{3}{2}B\psi^2 + 2C\psi^3 = 0 \quad (5.27)$$

From microscopic arguments, Wong is able to show that the order parameter here has a different meaning, namely that

$$|\psi|^2 \propto n_s^{3/2} \quad (5.28)$$

Consequently, if one assumes for the parameters  $A$  and  $B$  the temperature dependence

$$\begin{aligned} A(P,T) &= A_T \Delta T, \\ B(P,T) &= B_T \Delta T, \\ C(P,T) &> 0 \end{aligned} \quad (5.29)$$

one obtains  $n_s \propto (-\Delta T)^{2/3}$ . One thus obtains the proper dependence of superfluid density on temperature.

Again, one obtains a second-order phase transition for a bulk system. However, for a thin film, or for porous media, Wong obtains a third-order phase transition, which is indeed an improvement over the original Ginzburg-Pitaevski theory.

Wong has also applied his modified theory to the helium II film by assuming a suitable expression for the order function  $\psi$ . He then obtains

$$(\Delta T_\lambda) = - \frac{99.6}{[L(\text{\AA})]^2} \text{ } ^\circ\text{K} \quad , \quad (5.30)$$

which is in very good agreement with experimental results near the  $\lambda$ -point.





## 5.5 $T_\lambda$ DEPRESSION IN HELIUM II FILMS

In this section we shall present results of our calculations of the  $\lambda$ -temperature depression in films using four different criteria. This will tend to show that it is impossible to describe the observed depression in  $\lambda$ -temperature without considering in some way the surface effects. The calculations, though their merit is mainly of a qualitative rather than quantitative nature, will show that these surface effects become increasingly important as the thickness of the film is decreased. Moreover, the calculations are found to show a reasonable agreement with the experimental data concerning the specific heat maxima rather than with the data related to the breakdown of superflow in films.

The first criterion that we use for determining the transition temperature is simply to equate the inertial densities of all the excitations to the average total density of the film; for the latter we may assume the bulk density  $0.146 \text{ gm/cm}^3$  at  $T=2.2^\circ \text{K}$ . We know that this density varies by at most 7% between the transition temperature and absolute zero (22).

In order to calculate the inertial density of a gas of excitations we shall use Landau's definition (87) of inertial densities. According to this method, we give to the gas of excitations considered a drift velocity  $\mathbf{v}$  in a certain chosen direction, and calculate the resulting drift momentum  $\mathbf{J}$ . The inertial density  $\rho$  is then taken to be

$$\rho = \frac{J}{vV} \quad (5.31)$$

The drift momentum of a gas of excitations can be written as





$$J = \sum_{\underline{p}} \langle n_{\underline{p}} \rangle \underline{p} = \frac{1}{h^3} \int N(\underline{p}) \underline{p} d^3p d^3x, \quad (5.32)$$

where  $N(\underline{p})$  represents the appropriate occupation number for the excitation considered. The inertial densities of the elementary excitations are well-known but as an example we have calculated in Appendix B the inertial density of the quantized surface modes.

The inertial density of rotons turns out to be

$$\rho_{nr} = \frac{4\pi p_o^2 (2\pi\mu kT)^{1/2} e^{-\Delta/kT}}{3h^3 kT} \left\{ \mu kT + p_o^2 \right\}. \quad (5.33)$$

For phonons we obtain

$$\rho_{ph} = \frac{16\pi^5 k^4 T^4}{45h^3 c^3}, \quad (5.34)$$

which, at temperatures above 0.5°K is much smaller than the roton component.

In the case of ripplons we obtain the result

$$\frac{10\pi}{9h^2} \left( \frac{h\rho}{\sigma} \right)^{4/3} (kT)^{5/3} \Gamma\left(\frac{7}{3}\right) \zeta\left(\frac{7}{3}\right) \left(\frac{1}{t}\right), \quad (5.35)$$

which depends, of course, on the thickness  $t$  of the film.

When we set the sum of the inertial densities of the above excitations equal to the average film density we obtain the results given in Column 1 of Table 5.2. The  $\lambda$ -temperatures obtained for all film thicknesses are much higher than the experimental values obtained by Long and Meyer. Clearly we have not taken into account to a full extent all the surface factors present though the trend seems to be essentially right.

The next approach is somewhat related to that of Ginzburg and Pitaevski. Since the free energy per unit volume of



helium II is a continuous function of temperature even at the transition point, the  $\lambda$ -temperature corresponds to a definite value of the free energy per unit volume, i.e., the free energy of helium II must reach a definite value before the transition to the phase helium I occurs. We shall assume that this value of the free energy per unit volume must also be attained in the case of a helium II film in order that one arrives at the transition. In order to define a transition temperature in the film we may, therefore, equate the free energy per unit volume in the bulk system at  $T=2.18^\circ\text{K}$  to the free energy per unit volume of the helium II film at  $T=T_\lambda$ . Since surface effects in the film contribute considerably to the free energy,  $T_\lambda$  can be expected to be considerably modified in relation to the bulk value of  $2.18^\circ\text{K}$ .

For the time being we shall consider the free energy of the film to be made up of three parts, namely due to rotons, phonons and ripplons. Needless to say, it is only the phonon and roton contributions that are present in the free energy of the bulk system.

For the free energy of phonons, we substitute the relevant energy-momentum relation  $E=pc$  into the main term of Eq. (2.15), and obtain

$$\left(\frac{F}{V}\right)_{\text{ph}} = - \frac{8\pi \zeta(4) (kT)^4}{h^3 c^3} \quad . \quad (5.36)$$

In the case of rotons also we have to calculate the volume contribution to the free energy in a similar way as was done for the surface correction in 2.3, with the result that

$$\left(\frac{F}{V}\right)_r = - \frac{4\pi}{h^3} (2\pi\mu kT)^{1/2} kT e^{-\Delta/kT} [\mu kT + p_o^2] \quad . \quad (5.37)$$





Since the ripplon surface contribution has been shown to be much larger than the surface corrections to Eqs. (5.35) and (5.36), we can neglect these.

The ripplon contribution to the free energy of the film has already been calculated and is just given by Eq. (2.29),

$$\left(\frac{F}{V}\right)_s = - \pi \left(\frac{\rho'}{2\rho\sigma}\right)^{2/3} h \left(\frac{kT}{h}\right)^{7/3} \Gamma(7/2) \rho(7/3) \frac{1}{t} . \quad (5.38)$$

Hence we have to solve the equation

$$\left[\left(\frac{F}{V}\right)_{ph} + \left(\frac{F}{V}\right)_r\right]_{T = 2.18^\circ K} =$$

$$\left[\left(\frac{F}{V}\right)_{ph} + \left(\frac{F}{V}\right)_r + \left(\frac{F}{V}\right)_s\right]_{T = T_\lambda} \quad (5.39)$$

for various values of  $t$ . The results are given in Column 2 of Table 5.2, and are in somewhat better agreement with experiment than those in Column 1. It is clear, however, that there must be other factors present to depress the  $\lambda$ -temperature even further. This bears out the statement of Atkins (89) that the lowering of the  $\lambda$ -point in thin films cannot be due solely to ripplons.

However, we have already remarked in Chapter 3 also that the decrease with temperature of the surface tension of helium II cannot be explained solely in terms of the ripplon contribution, as calculated by Atkins (22). This may be due to two reasons:

- 1) the contribution of the quantized surface waves to the free energy of the surface may not have been taken into account properly, or
- 2) there are additional surface excitations present which contribute to the surface free energy.





Atkins (22) and Lovejoy (41) have given several reasons for believing that the surface wave contribution has not sufficiently been taken into account. These reasons have been reviewed in 3.4. Whichever of the alternatives is true, the total surface contribution to the free energy can be taken into account by taking as the free energy due to surface excitations the experimentally determined result of Atkins and Narahara (21) which is just

$$\left(\frac{F}{V}\right)_s = \frac{-0.0081 T^{2.5}}{t} \quad (5.40)$$

If we substitute this into equation (5.38) in place of the ripplon contribution alone (Eq. 5.40) will include the ripplon component) we obtain the results given in Column 3 of Table 2.4. These results are in much better agreement with experiment.

Next, we may include into our equation a free energy contribution arising from excitations near the wall. Here the van der Waals attraction between the helium atoms and the wall causes a nonuniformity of density, as shown in Appendix II. We have presented there a calculation estimating the free energy due to such a non-uniformity. If we assume that the creation of excitations with increase in temperature causes the helium film to be less loosely bound at higher temperatures, and moreover that these excitations have an energy spectrum similar to the surface excitations, then we obtain a further contribution to the free energy of the film of the amount

$$\left(\frac{F}{V}\right)_w = - 0.0020 T^{2.5} \quad (5.41)$$

Taking this into account and again using Eq. 5.38 as our basic equation, we obtain the results shown in Column 4 of Table 5.2.



Table 5.2

Comparison of theoretical estimates of the  $T_{\lambda}$ -depression with experimental data.

Thickness $A$ in $\text{\AA}$	Renormalized Temperatures in $^{\circ}\text{K}$				Experimental Value of $T_{\lambda}$
	$T_1$	$T_2$	$T_3$	$T_4$	
0	0	--	0	0	-
10	2.05	1.81	1.66	1.56	1.46
25	2.11	2.02	1.97	1.89	1.83
60	2.16	2.12	2.09	2.07	2.14
750	2.18	2.18	2.18	2.18	2.18
Bulk	2.18	2.18	2.18	2.18	2.18

The results appear to confirm our procedure of taking into account the surface effects in helium films. However, there are several points that must be noted here:

1) For thick films the effects due to the non-uniform regions at the free surface and near the wall have been rather overstated. When the film is thick enough the central layers of the film can be considered in a sense independent from the "surface" layers and hence superfluidity might occur in the bulk of the film at temperatures higher than the ones calculated in column 4.

2) In the thin film region the experimental values lie below the calculated ones. One reason for this is that we have treated the roton-like excitations as mutually noninteracting. It is clear, however, that the various excitations interact



strongly at temperatures above  $1^{\circ}\text{K}$ . Secondly, and equally significantly, we have ignored the finite-size effects upon the energy spectrum of the excitations (47,90). The true  $\lambda$ -point depression can probably only be explained satisfactorily if both surface effects and finite size effects are taken into account together.

3) The measurable "transition temperatures" in helium films are (i) the onset temperatures for superflow and (ii) the temperature at which the specific heat of the system is maximum. Hence, an important improvement in the above discussion would be a calculation of the specific heat maximum from a better knowledge of the energy spectrum of the excitations.

4) One could also do the calculations considering the first layer from the wall to be solid, as done by Brewer et al (66), in which case agreement with experiment would be better for thin films. However, as there is as yet little agreement on this question (67) there is not much point in doing such a calculation at present.

Nevertheless it appears to have been demonstrated fairly conclusively that the surface effects are of extreme importance in films in understanding the physical behaviour of helium films.





## CHAPTER 6

### DEPRESSION OF TRANSITION TEMPERATURE IN ROTATING HELIUM II

#### 6.1 INTRODUCTION

In view of the depression of the transition temperature in helium II films and in porous media, it is imperative that one consider the nature of the superfluid phase transition in rotating helium II. A depression in the lambda temperature of rotating helium II can certainly be predicted theoretically. However, since the size of the rotating cylindrical container is characteristically much larger than the corresponding thickness of the helium II film, it will be evident that the mechanism responsible for the depression of the transition temperature in rotating He II differs in nature from the corresponding mechanism in He II films. For the same reason, the depression in transition temperature will be much smaller in the case of the rotating He II. In fact, experiments to this date have not yet been able to measure the lambda temperature of helium in rotation to a sufficiently great degree of accuracy in order to detect such a small effect. Before going into more detail, however, we shall review some of the relevant properties of helium II in a rotating medium.

As is well-known, when a cylindrical vessel containing helium II is set into uniform rotation, the whole of the fluid appears to imitate solid-body rotation. This was contrary to the prediction of the Landau theory (88) according to which the absence of viscosity in the superfluid component, and the necessity of maintaining potential motion (i.e.  $\text{curl } \underline{v}_s = 0$ ), the superfluid component would not partake in





the rotational motion of the vessel and hence only the normal component of the liquid would rotate. The first experiment to test this prediction was performed by Osborne (89) in 1950. The results showed that helium II rotated as a whole; so it was thought that the interaction of the superfluid component with the walls of the vessel or with the normal component must be responsible for this "breakdown" of superfluidity. However, an earlier experiment performed by Andronikashvili (90) in 1946, concerned with axial oscillations of a pile of closely spaced parallel thin discs had shown that superfluidity was not destroyed by rotation but that only the normal component was dragged into rotation. A later experiment (Andronikashvili and Kaverkin (91)) in 1955 showed that the fountain effect continued to exist in rotating helium II and had, in fact, the same quantitative features as in helium II at rest. As a result of these experiments it became evident that, although an interaction did exist between the superfluid and normal components of rotating helium II, this interaction was not related to the breakdown of superfluidity. In accordance with Onsager's hypothesis (92) in 1949, this interaction was related to the appearance of vortex lines in the superfluid component of helium II. The circulation of these vortices was quantized in units of  $h/m$ . This quantization of the circulation explains the existence of an initial critical velocity  $\omega_{c_1}$  below which the superfluid component does not at



all participate in the rotation. For if a vortex line cannot exist in a state with arbitrarily small intensity, then vortex formation can take place only if some minimum energy is available in the fluid flow. Superfluidity, on the other hand, is destroyed only when some greater critical velocity,  $\omega_{c_2}$  say, is reached.

Experimental as well as theoretical evidence for the existence of vortices in rotating helium II was quickly forthcoming. In 1955, Feynman used quantum mechanical ideas to explain the possibility of vortex formation in liquid helium and showed that the established fact of superfluid rotation is adequately explained by the existence of quantized vortices. The macroscopic velocity field formed by these vortices for each velocity of rotation simulates that of a classical fluid. This in turn defines at all velocities of rotation an equilibrium density of vortex lines in the rotating fluid. Experimental evidence for the existence of quantized circulation came from the classic experiments of Vinen (93) who utilized the existence of a Magnus force between a vortex line and a vibrating wire to demonstrate that circulation did appear in quanta of  $h/m$ .

The first experiment designed to study a possible shift in transition temperature of rotating liquid helium was performed by Zamtaradze and Tsakadze (94) in 1964. They studied the nature of the thermomechanical effect near the transition point in order to determine the effect of a uniform





angular velocity  $\omega$  on the phase transition. They found that the dependence of the height of superfluid helium on its temperature does not differ significantly from that of the fluid at rest.

Bablidze, Tsakadze and Cheishvili (95) performed an experiment, again in 1964, which was designed to observe the discontinuity in the heating or cooling curve at the transition temperature of a phosphor-bronze thermometer placed in rotating helium and then compared it with the corresponding situation for liquid helium at rest. This break in the heating or cooling curve is connected with a jump taking place in the thermal resistivity when helium II passes through the transition into helium I and vice versa. In this experiment, where the maximum attainable angular velocity was  $\omega = 0.54 \text{ sec}^{-1}$ , no shift of the transition temperature to within the experimental accuracy of  $5 \times 10^{-4} \text{ }^\circ\text{K}$  was observed.

Theoretical estimates of the lambda temperature depression in rotating helium II have been made on the basis of the Ginzburg-Pitaevski model of helium II. Kiknadze, Mamaladze and Cheishvili (98) have considered solutions of the equation

$$\frac{1}{2m} \{i \frac{\hbar}{m} \nabla + \underline{\omega} \times \underline{r}\}^2 \Psi - \alpha \Psi + \beta |\Psi|^2 \Psi = 0, \quad (6.1)$$

which represents a generalization of the Ginzburg-Pitaevski





equation with  $\underline{v}_n = \underline{\omega} \times \underline{r}$ , i.e., the normal fluid is in uniform rotation. This equation admits solutions describing a unit vortex line in an infinite liquid. As  $x \rightarrow 0$ , the function  $\psi$  is of the form  $cx$ . For  $x \gg \ell$ , Eq. (6.1), with  $\underline{\omega} = 0$ , has the asymptotic solution

$$\psi \approx 1 - \frac{\ell^2}{x^2}$$

where  $\ell = \hbar / \sqrt{2m\alpha}$ . This solution represents a vortex line in which the density at the vortex core equals zero and rises to the normal fluid density at a distance of the order of the healing length  $\ell$ . Kiknadze, Mamaladze, and Cheishvili have shown that Eq. (6.1) also has solutions corresponding to the presence of a vortex line with the expected difference that the vortex axis moves with the normal component of the fluid. In fact, analogous to the two-dimensional array of magnetic field lines in Type II superconductors, as determined by Abrikosov (96) in 1957, Eq. (6.1) also admits of stable arrays of triangular and square lattices of vortex lines.

The possibility of the destruction of superfluidity is realized in the case of an infinite fluid moving with velocity  $\omega = \omega_{c_2}$ . As  $\omega \rightarrow \omega_{c_2}$ , the wavefunction of He II, obtained as a solution of Eq. (6.1), tends to zero smoothly. This leads to an approximate shift in the transition temperature as given by [10]

$$\Delta T_\lambda \approx -(2.3 \times 10^{-11}) \omega \quad ^\circ\text{K}, \quad (6.2)$$



where  $\omega$  is measured in rad/sec.

Kiknadze, Mamaladze and Cheishvili (98) have also determined approximately the values of the critical velocity of rotation at which the superfluid density in a vessel of finite size becomes zero. One thereby obtains

$$\Delta T_{\lambda} \approx -(1.1 \times 10^{-14}) / R^2 \text{ } ^\circ\text{K}, \quad (6.3)$$

where  $R$  is measured in cm. This relation is valid only for a small range of angular velocities just above  $\omega_{c_1}$ . As  $\omega$  is further increased,  $\Delta T_{\lambda}$  will depend on both  $\omega$  and  $R$  until the critical velocity  $\omega_{c_2}$  for the breakdown of superfluidity is reached.

In the next two sections, we present a calculation of the depression of the transition temperature in rotating liquid helium. The functional dependence of the  $T_{\lambda}$ -depression on the angular velocity as well as the radius of the (cylindrical) container will be derived. Further, we will obtain as special cases of our more general result two relations which are practically the same as relations (6.2) and (6.3).



## 6.2 INERTIAL DENSITY OF A ROTATING GAS OF EXCITATIONS

Our approach consists in calculating the inertial density of a rotating gas of excitations (phonons and rotons) as a function of the angular velocity  $\omega$ , the radius  $R$  of the cylindrical container, and the temperature  $T$ . This will naturally represent the density  $\rho_n(T)$  of the normal component of the fluid. The temperature at which this density becomes equal to the total density  $\rho$  of the liquid helium, i.e., when  $\rho_s = 0$ , we will take as the transition temperature. Thus a relationship can be obtained between the transition temperature  $T_\lambda$  and the parameters  $\omega$  and  $R$ .

We employ as before Landau's definition (85) of the inertial density of elementary excitations for calculating the inertial density of a rotating gas of phonons and rotons. To do this, we study the gas of excitations from a frame of reference in which it appears to have a mass-motion characterized by a drift velocity  $\underline{v}$  and calculate the accompanying drift momentum  $\underline{J}$ . The inertial density  $\rho$  is then given by the obvious formula

$$\rho = \frac{\underline{J}}{\underline{v} V}, \quad (6.4)$$

where  $V$  is the volume of the gas.

The drift momentum of the gas can be written as

$$\underline{J} \equiv \sum_{\underline{p}} \langle n_{\underline{p}} \rangle \underline{p} = \frac{1}{h^3} \int n(\underline{p}; \underline{v}, \omega) \underline{p} d^3x d^3p, \quad (6.5)$$





where  $n(\underline{p}; \underline{v}, \underline{\omega})$  is the relevant mean occupation number. For rotons we have

$$n(\underline{p}; \underline{v}, \underline{\omega}) = \left[ \exp \left\{ \beta (E_{\underline{p}} - \underline{v} \cdot \underline{p} - \underline{\omega} \cdot \underline{l}) \right\} - 1 \right]^{-1}$$

$$\approx \exp \left\{ -\beta (E_{\underline{p}} - \underline{v} \cdot \underline{p} - \underline{\omega} \cdot \underline{l}) \right\}, \quad (6.6)$$

where  $E_{\underline{p}} = \Delta + (p - p_0)^2 / 2\mu$ , and  $\beta = 1/kT$ , and  $l$  is the angular momentum of an excitation. Carrying out the Taylor expansion of (6.6) about  $(\underline{v}, \underline{\omega}) = (0, 0)$ , we can write

$$n(\underline{p}; \underline{v}, \underline{\omega}) = n(\underline{p}) \left\{ 1 - \beta \delta E + \frac{\beta^2}{2!} (\delta E)^2 - \frac{\beta^3}{3!} (\delta E)^3 + \dots \right\} \quad (6.7)$$

where  $\delta E = -(\underline{v} \cdot \underline{p} + \underline{\omega} \cdot \underline{l})$ . The even-order terms of this expansion do not contribute to the drift momentum (6.5) because in their case the integrand becomes an odd function of the momenta. The first two odd-order terms yield the following result:

$$\underline{J} = \overline{N}_r p_0 \left[ \frac{1}{3} \frac{p_0 v}{kT} + \frac{1}{30} \frac{p_0^3 v}{(kT)^3} \left\{ v^2 + \frac{1}{2} (\omega^2 R^2) \right\} + \dots \right], \quad (6.8)$$

where  $R$  is the radius of the cylindrical enclosure and  $\overline{N}_r$  the mean number of rotons in the gas at rest. For the



inertial density of the roton gas, we thus obtain

$$\rho_r(v, \omega) = \rho_r(0, 0) \left[ 1 + \frac{1}{10} \left( \frac{p_o}{kT} \right)^2 v^2 + \frac{1}{20} \left( \frac{p_o^R}{kT} \right)^2 \omega^2 + \dots \right]. \quad (6.9)$$

It may be pointed out here that the first two terms in this expansion are just the first two terms of the general expansion for  $\rho_r(v)$  as given by Khalatnikov (99):

$$\rho_r(v) = 3 \left( \frac{kT}{p_o v} \right)^2 \rho_r(0) \left[ \cosh \left( \frac{p_o v}{kT} \right) - \left( \frac{kT}{p_o v} \right) \sinh \left( \frac{p_o v}{kT} \right) \right]. \quad (6.10)$$

In the case of phonons, the relevant occupation numbers are

$$n(\underline{p}; \underline{v}, \underline{\omega}) = \left[ \exp \left\{ \beta (E_{\underline{p}} - \underline{v} \cdot \underline{p} - \underline{\omega} \cdot \underline{\ell}) \right\} - 1 \right]^{-1}, \quad (6.11)$$

where  $E_{\underline{p}} = pc$ ,  $c$  being the velocity of sound in the liquid. The integration (6.5) is once again straightforward, though somewhat laborious, with the result

$$\rho_{ph}(v, \omega) = \rho_{ph}(0, 0) \left[ 1 + \frac{3v^2}{c^2} + \frac{R^2}{c^2} \omega^2 + \dots \right] \quad (6.12)$$

It again may be pointed out that the first two terms of this expansion are just the first two terms of the general expression for  $\rho_{ph}(v)$ , as given by London (100)

$$\rho_{ph}(v) = \rho_{ph}(0) \left[ 1 - \frac{v^2}{c^2} \right]^{-3}. \quad (6.13)$$



In the limit  $v \rightarrow 0$ , we get

$$\rho_r(\omega) = \rho_r(0) \left[ 1 + \frac{1}{20} \left( \frac{p_o R}{kT} \right)^2 \omega^2 + \dots \right], \quad (6.14)$$

and

$$\rho_{ph}(\omega) = \rho_{ph}(0) \left[ 1 + \frac{R^2}{c^2} \omega^2 + \dots \right]. \quad (6.15)$$

Since we shall be concerned only with temperatures in the neighborhood of  $T=T_\lambda$ , the inertial density of the phonons can be shown to be much smaller than the inertial density of the rotons and may, therefore, be neglected. However, for typical values of the parameters involved, viz.  $R = 1\text{cm}$ , and  $\omega = 30\text{rad/sec.}$ , the change  $\Delta\rho_r$  in inertial density of the normal fluid can become quite appreciable. In fact, for  $T_{\lambda_0} \approx 2.18^\circ\text{K}$ , we have a relative density increase as high as

$$\frac{\Delta\rho_r}{\rho_r(0)} \approx 1 \times 10^{-5}. \quad (6.16)$$





### 6.3 DEPRESSION OF TRANSITION TEMPERATURE IN ROTATING HELIUM II

Although ~~pyc~~enometric studies by Andronikashvili and Tsakadze (101) had apparently shown an anomalous increase in the density of helium II when brought into rotation, of a magnitude comparable to that given by Eq. (6.16), more recent experiments by Esel'son et al (102-105) have almost conclusively proved that, when sufficient care is taken to ensure temperature stability in the rotating fluid, one does not observe any density changes to within an accuracy of 1 in  $2 \times 10^6$ . It is clear then that Eqs. (6.14) and (6.15) represent an increase in the density of the normal fluid at the expense of the superfluid component. Consequently, the calculation outlined in Section 6.2 is valid only when the superfluid component itself is in rotation, i.e., for  $\omega_{c_1} \leq \omega \leq \omega_{c_2}^*$ .

In order to study the behaviour of the transition temperature  $T_\lambda$  we set the roton inertial density (6.14) equal to the corresponding quantity for non-rotating helium at the transition point  $T_{\lambda_0}$ . We then obtain, using Eq. (4.32),

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\* The condition  $\omega \leq \omega_{c_2}$  is necessary to safeguard the situation against a total breakdown of superfluidity.



$$\frac{e^{-\Delta/kT_{\lambda_0}}}{T_{\lambda_0}^{1/2}} \approx \frac{e^{-\frac{\Delta}{kT_{\lambda}}}}{T_{\lambda}^{1/2}} \left\{ 1 + \frac{1}{20} \left( \frac{p_0 R}{kT_{\lambda}} \right)^2 \omega^2 + \dots \right\} \quad (6.17)$$

Rearranging (6.17) in order to solve for  $\Delta T_{\lambda} (= T_{\lambda} - T_{\lambda_0})$ , the depression in the lambda temperature, and retaining only the first two terms of the exponential, we obtain for the  $T_{\lambda}$  depression

$$\Delta T_{\lambda} \approx - \frac{1}{20(\Delta/k)} \left( \frac{p_0}{\hbar} \right)^2 \omega^2 R^2. \quad (6.18)$$

Substituting for the relevant numerical factors one obtains the final result

$$\Delta T_{\lambda} \approx -(1.25 \times 10^{-8}) \omega^2 R^2 \text{ } ^\circ\text{K}, \quad (6.19)$$

where  $\omega$  and  $R$  are measured in rad/sec. and cm respectively.

As pointed out earlier, this formula is valid for the range of angular velocities in which the superfluid is dragged into rotation. Blatt and Butler (106) have shown that the first internal energy jump in an ideal Bose gas contained in a cylindrical vessel of radius  $R$  takes place at an angular velocity

$$\omega_{c_1} = 4.45 \hbar / mR^2. \quad (6.20)$$

This is comparable in value to the critical velocity for the creation of a vortex line as found by Arkhipov (107) and



Vinen (93):

$$\omega_{c_1} \approx \frac{\hbar}{m} (R^2 - a^2)^{-1} \ln \left( \frac{R}{a_0} \right), \quad (6.21)$$

where  $a_0$  is the core radius of the vortex. Starting from this velocity the creation of vortex lines is thermodynamically favourable. As the angular velocity increases, the number of vortex lines increases until a maximum number of vortex lines is reached at an angular velocity  $\omega_{c_1}' \approx 4\omega_{c_1}$  (98).

Hence the angular velocities for which the formula (6.19) for the  $T_\lambda$ -depression is valid are confined to a narrow interval of angular velocities

$$\omega \gtrsim \frac{4.45\hbar}{mR^2}. \quad (6.20)'$$

Substituting this value of  $\omega$  into equation (6.19) we obtain for the dependence of  $\Delta T_\lambda$  on  $R$

$$\Delta T_\lambda \approx -(0.9 \times 10^{-14}) / R^2 \text{ } ^\circ\text{K}, \quad (6.22)$$

which is in excellent agreement with the corresponding result of Kiknadze et al (12):

$$\Delta T_\lambda \approx -(1.1 \times 10^{-14}) / R^2 \text{ } ^\circ\text{K}. \quad (6.22a)$$

If, on the other hand, we decide to keep the radius  $R$  constant,





and vary the angular velocity  $\omega$ , then we can obtain the desired result by eliminating  $R$  between (6.19) and (6.20)':

$$\Delta T_{\lambda} \approx -(1.7 \times 10^{-11}) \omega \text{ }^{\circ}\text{K} , \quad (6.23)$$

which is again in good agreement with the corresponding result of Kiknadze and Mamaladze (12):

$$\Delta T_{\lambda} \approx -(2.3 \times 10^{-11}) \omega \text{ }^{\circ}\text{K}. \quad (6.23a)$$

One must indeed remember that the two relations (6.22) and (6.23) are valid only for constant values of  $\omega$  and  $R$  respectively. When both the angular velocity and the size of the container are allowed to vary, Eq. (6.19) must clearly be used and a reliable estimate of the lambda temperature depression obtained.



## CHAPTER 7

### THE HELIUM FILM PROFILE

#### 7.1 INTRODUCTION

A large number of experiments have been performed in order to determine the thickness of saturated and unsaturated helium films at various heights. However, due to the difficulty of guarding against small amounts of radiation influx which greatly influence the amount of evaporation from the film, experimental results have not been generally in agreement.

Atkins (108) was the first to carry out a systematic measurement of the thickness of a saturated helium film by means of a dynamical method and established the empirical relation

$$d = 1.67 \times 10^{-6} / H^{1/7}, \quad (7.1)$$

where both  $d$  and  $H$  are measured in cm.

In a series of experiments, Burge and Jackson (109) and Jackson and Henshaw (110) have found the empirical result to be

$$d = 2 \times 10^{-6} / H^{1/3}. \quad (7.2)$$

However, when radiation was permitted to impinge on the top of the film, a variation approaching that of Atkins was obtained. It thus appears that Atkins' result was not reliable due to the radiation influx occurring.

An experiment by Bowers (111) in 1953 showed a still different variation of thickness versus height, namely

$$d = 11.8 \times 10^{-6} / H^{1/2}. \quad (7.3)$$



In a similar experiment on thin unsaturated films, Bowers found the relation (112)

$$d = 5 \times 10^{-6} / H^{1/3}. \quad (7.4)$$

Keeping in mind the possible relation between saturated and unsaturated films, as pointed out by Rice and Widom, this result is reasonable agreement with the relation obtained by Jackson et al.

The earliest theoretical work on the subject was done by Schiff (113) and Frenkel (114), who took into account the nature of the van der Waals force of attraction between the wall and the adsorbed helium atoms and derived the relation

$$d = (4 \times 10^{-6}) / H^{1/3}, \quad (7.5)$$

in the case of a helium film on a glass wall. The constant would, of course, vary with the material of the wall. This relation is in good agreement with the results of Jackson and coworkers on saturated films and with the work of Bowers on unsaturated films except that the temperature dependence of the constant  $k$  in the relation  $d = k/H^{1/2}$  could not be determined theoretically whereas the experimental value varied considerably with temperature.

A different theoretical approach was adopted by Bijl, de Boer, and Michels (115) who considered the variation of the zero point energy of the film with thickness. They visualized





the eigenfunctions of lowest energy as having nodes at the wall and at the free surface of the film and having wavelength  $\lambda = 2d$ , thus giving a zero point energy per atom

$$Z = \frac{h^2}{8md^2} \quad (7.6)$$

Minimizing the sum of the zero point energy and the gravitational energy one obtains the relation

$$d = \frac{h}{2m} \cdot \left(\frac{1}{2gH}\right)^{1/2} \approx \frac{1 \times 10^{-5}}{H^{1/2}} \quad (7.7)$$

This agrees well with the work of Bowers on thick saturated films. The drawback in this method is that, with the eigenfunctions considered, it leads to a concentration of helium atoms toward the middle of the film which is physically unrealistic. However, as the result agrees with a number of experiments, it seems that the correct relation between thickness and height might be of the form

$$d = k_1/H^{1/3} + k_2/H^{1/2}. \quad (7.8)$$

In this chapter we shall discuss the various attempts that have been made to derive a relation of the form (7.8). In both these attempts the effect of the finite film thickness on the zero point energy of the helium film is calculated, and its influence on the d-H relationship studied. A comparison of



the results obtained by different approaches makes quite an interesting study.

The main result of this discussion, however, will be a vindication of the contention made by Pathria (25), namely that, if the expression for the density of single-particle states is written as

$$g(K) = \frac{K^3}{6\pi^2} V + \frac{K^2}{6\pi} S + E(K),$$

then the error term is  $o(K^2)$  and not  $O(K^2)$ , i.e. the error term is of an order inferior to that of the surface term. In his paper, Pathria has provided computational evidence in favor of the contention. Here we shall obtain further evidence in favour of this contention. To do this, we will present a calculation for the thickness dependence of the zero point energy of the film, not only for the Neumann boundary conditions as was done by Atkins, but also for Dirichlet and periodic boundary conditions. The results will show that, as was contended by Pathria, the error term in the expression for  $g(K)$  is definitely inferior to the surface term.



## 7.2 ZERO POINT ENERGY OF A HELIUM FILM

After Atkins, we assume the zero point energy of a helium film of thickness  $d$  to be of the form

$$Z(d) = Z(\infty) \left[ 1 + \frac{a_1}{d} + \frac{a_2}{d^2} + \dots \right], \quad (7.8)$$

where  $Z(d)$  is the zero point energy per gram of a film of density  $\rho$  and  $Z(\infty)$  is the zero point energy per gram for the bulk liquid.

Imagine a film of unit area at a height  $H$  above the bulk liquid and consider an increase in its thickness from  $d$  to  $d + t$ . The change in the energy of the system is then

$$\begin{aligned} \Delta U = \rho t (gH - \frac{\alpha}{d^3}) + \rho t \frac{\partial}{\partial d} \left[ d Z(\infty) \left( 1 + \frac{a_1}{d} + \frac{a_2}{d^2} + \dots \right) \right] \\ - \rho t Z(\infty). \end{aligned}$$

In equilibrium  $\Delta U$  should be zero and hence

$$H = \frac{\alpha}{gd^3} + \frac{Z(\infty)}{g} \left[ \frac{a_2}{d^2} + \frac{a_3}{d^3} + \dots \right]. \quad (7.9)$$

We now calculate that part of the zero point energy that arises from longitudinal Debye waves. In a square film of side  $L$  cm. and thickness  $d$  cm. a typical Debye wave of frequency  $\nu$  and velocity  $c$  has direction cosines  $l_x$ ,  $l_y$ , and  $l_z$  given by

$$l_x = \frac{n_x c}{2L\nu}, \quad l_y = \frac{n_y c}{2L\nu}, \quad l_z = \frac{n_z c}{2d\nu},$$





$n_x, n_y, n_z$  being integers. Hence the lattice points corresponding to waves with frequencies not exceeding a given frequency  $\nu$  will lie in a region bounded by the ellipsoid

$$\frac{n_x^2 + n_y^2}{L^2} + \frac{n_z^2}{d^2} = \frac{4\nu^2}{c^2} \quad (7.10)$$

The length  $L$  of a side can be made very large permitting large values of  $n_x$  and  $n_y$ , but, if  $d$  is small, the maximum possible value for  $n_z$  is  $m = \frac{2d\nu_c}{c}$  where  $\nu_c$  is the cutoff frequency. We choose  $d$  so that  $m$  is an integer. Then, for a fixed value of  $n_z$  the number of modes with frequency between  $\nu$  and  $\nu+d\nu$  will be

$$g(n_z, \nu) d\nu = \frac{2\pi L^2}{c^2} \nu d\nu,$$

but with a minimum value  $\nu_{\min} = \frac{n_z c}{2d}$ .

The cutoff frequency can be calculated by equating the total number of modes of vibration to  $N$ , the total number of particles in the film.

$$\begin{aligned} N &= \sum_{n_z=0}^{n_z=m} \int_{\nu_{\min}}^{\nu_{\max}} g(n_z, \nu) d\nu \\ &= \frac{\pi L^2}{c^2} \sum_{n_z=0}^m \left[ \nu_c^2 - \frac{c^2 n_z^2}{4d^2} \right] \\ &= \frac{\pi L^2}{c^2} \left[ (m+1) \nu_c^2 - \frac{1}{6} m(m+1)(2m+1) \frac{c^2}{4d^2} \right] \end{aligned}$$



for Neumann boundary conditions, and

$$= \frac{\pi L^2}{c^2} m \gamma_c^2 - \frac{1}{6} m(m+1)(2m+1) \frac{c^2}{4d^2}$$

for Dirichlet boundary conditions. Inserting  $m = \frac{2dv_c}{c}$  and solving for  $v_c$  in terms of  $v_c^\infty$ , we obtain

$$v_c = v_c^\infty \left[ 1 + \frac{1}{4} \frac{c}{2v_c^\infty d} + \frac{7}{48} \left( \frac{c}{2v_c^\infty d} \right)^2 + \dots \right], \quad (7.11)$$

where  $v_c^\infty$  is the cutoff frequency for the bulk liquid and the upper sign corresponds to Neumann boundary conditions.

The zero point energy can now be calculated,

$$\begin{aligned} L^2 \rho d Z(d) &= \sum_{n_z=0}^m \int_{v_{\min}}^{v_{\max}} \frac{1}{2} h v g(n_z, v) dv \\ &= \frac{\pi L^2}{3dc^2} \sum_{n_z=0}^m \left[ v_c^3 - \left( \frac{c}{2d} \right)^3 n_z^3 \right] \\ &= \frac{\pi L^2 h}{3dc^2} \left[ (m+1) v_c^3 - \frac{1}{4} m^2 (m+1)^2 \frac{c^3}{8d^3} \right] \end{aligned}$$

for Neumann boundary conditions, and

$$= \frac{\pi L^2 h}{3dc^2} \left[ m v_c^3 - \frac{1}{4} m^2 (m+1)^2 \frac{c^3}{8d^3} \right]$$

for Dirichlet boundary conditions.

Substituting for  $m = \frac{2dv_c}{c}$ , we obtain for the zero point energy



$$Z(d) = \frac{\pi h}{3dc^2\rho} \left[ \frac{3}{2} \frac{d}{c} v_c^4 \pm \frac{1}{2} v_c^3 - \frac{1}{4} \left( \frac{c}{2d} \right) v_c^2 + \dots \right],$$

and using relation (7.11) for  $v_c$ , we have finally

$$Z(d) = Z(\infty) \left[ 1 \mp \frac{1}{6} \left( \frac{c}{v_c^\infty d} \right) + \frac{1}{32} \left( \frac{c}{v_c^\infty d} \right)^2 \pm \frac{25}{384} \left( \frac{c}{v_c^\infty d} \right)^3 + \dots \right]. \quad (7.12)$$

Substituting this expression into equation (7.9) we obtain

$$H = \frac{\alpha}{gd^3} + \frac{Z(\infty)}{32g} \left( \frac{c}{dv_c^\infty} \right)^2, \quad (7.13)$$

irrespective of the boundary conditions used. Inserting the relevant numbers, this gives

$$H = \left( \frac{4 \times 10^{-6}}{d} \right)^3 + \left( \frac{4 \times 10^{-6}}{d} \right)^2. \quad (7.14)$$

For thin films this agrees with the experimental findings of Bowers (112) for the unsaturated films and with Jackson's results (109, 110) for the saturated films. For thick films, however, the zero point energy term becomes more important and hence in the expression  $d = k/H^{1/n}$ ,  $n$  would begin to approach 2. For thick films, then, this result agrees fairly well with the experimental results of Bowers (111) on saturated films.

In the case of periodic boundary conditions the wavefunctions will have the form

$$\psi_{lmn}(r) \propto e^{i\mathbf{k} \cdot \mathbf{r}}$$



where  $\bar{k} = (\frac{1}{a}, \frac{m}{b}, \frac{n}{d})$ . Again, the points of interest are contained in the ellipsoid

$$\frac{v^2}{c^2} = \frac{\ell^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{d^2}.$$

Choosing  $a = b = L$ , this corresponds to the ellipsoid

$$n_x^2 + n_y^2 = L^2 \left[ \frac{v^2}{c^2} - \frac{n_z^2}{d^2} \right].$$

Again,  $L$  can be made as large as we like, but the maximum value of  $n_z$  is now  $m = \frac{d}{c} v_c$ .

The number of modes with frequency between  $v$  and  $v+dv$  is  $A v dv$  with the minimum value of  $v$  being  $\frac{c}{d} n_z$ .

Evaluating the cutoff frequency again, we obtain

$$\begin{aligned} N &= A \sum_{n_z=-m}^m \int_{v_{\min}}^{v_{\max}} v dv \\ &= A' \left[ v_c^3 - \frac{1}{4} \left( \frac{c}{d} \right)^2 v_c \right] \end{aligned} \quad (7.15)$$

Solving for  $v_c$  in terms of  $v_c^\infty$ , we have

$$v_c = v_c^\infty + \frac{1}{12} \left( \frac{c}{d} \right)^2 \frac{1}{v_c^\infty} \quad (7.16)$$





We now calculate the zero point energy as before

$$\begin{aligned}
 Z(d) &= B \sum_{n_z=-m}^m \int_{\gamma_{\min}}^{\gamma_{\max}} \left( \frac{1}{2} h \gamma \right) \gamma d\gamma \\
 &= B' \sum_{n_z=-m}^m \left[ \gamma_c^3 - \left( \frac{c}{d} \right)^3 |n_z|^3 \right] \\
 &\Rightarrow B'' \left[ \gamma_c^4 - \frac{1}{3} \left( \frac{c}{d} \right)^2 \gamma_c^2 \right] .
 \end{aligned} \tag{7.17}$$

Substituting (7.16) into (7.17) we obtain the final result

$$Z(d) = Z(\infty) \left[ 1 + \frac{1}{24} \left( \frac{c}{d} \right)^4 + \dots \right] . \tag{7.18}$$

This is, of course an expected result. Finite size effects cannot be taken into account properly if periodic boundary conditions are adopted.

We can use the foregoing result to check the accuracy of the density of states relation (2.2). If we do the calculation using the density of states approach, we have

$$g(\gamma) d\gamma = \frac{4\pi V}{c^3} \gamma^2 d\gamma + \frac{\pi S}{2c^3} \gamma d\gamma + \dots$$

For the zero-point energy in the first approximation we obtain in a straightforward way



$$\begin{aligned}
 Z(d) &= \int_0^{\gamma_c} \left( \frac{1}{2} h \gamma \right) g(\gamma) d\gamma \\
 &= \frac{4\pi V}{c^3} \frac{1}{2} h \int_0^{\gamma_c} \gamma^3 d\gamma + \frac{\pi S h}{4c^2} \int_0^{\gamma_c} \gamma^2 d\gamma \\
 &= \frac{\pi h V \gamma_c^4}{2c^3} + \frac{\pi S h}{12c^2} \gamma_c^3 + \dots
 \end{aligned}$$

Hence

$$Z(d) = Z(\infty) \left[ 1 + \frac{1}{6} \left( \frac{c}{\gamma_c^\infty d} \right) + \dots \right] . \quad (7.21)$$

This result is in exact agreement with Eq.(7.12); hence  $E(K) = o(K^2)$  and not  $O(K^2)$  and Pathria's contention appears to be borne out. Still further evidence for the correctness of Pathria's contention can be obtained from a calculation by Brouwer and Pathria (118). They derive an expression for the free energy of ideal Bose-Einstein gas particles by means of the density of states formula (2.2) and also by performing the summation over states directly by means of a method introduced by Fowler and Jones (118). Complete agreement is found up to the surface term. Franchetti(117) and Singh and Pathria(119) have also calculated the free energy of ideal gas particles and of phonons by constructing the Mellin transforms of the relevant summands and have obtained complete agreement with the results obtained by using the density of states formula.



In the case of periodic boundary conditions, the result obtained by using the density of state formula is just the first term of Eq. (7.21), with the surface term being zero. Hence agreement is obtained in this case also.

In passing, we may mention that Franchetti(117) has also calculated the thickness dependence of the zero-point energy of a film. He introduces two methods for calculating the zero point energy correction in films and his result differs considerably from that of Atkins. By a more approximate method Franchetti obtains

$$Z(d) \approx Z(\infty) \left[ 1 + \frac{1}{72} \left( \frac{c}{d\gamma_{\infty}^c} \right)^2 + \dots \right] . \quad (7.19)$$

Franchetti does not obtain a term proportional to  $1/d$  because, when summing over all frequencies, a contour is chosen so that the density of points is not altered. However, Franchetti obtained the above result by letting the total number of modes of vibration equal to  $3N$ . In a liquid, however, only longitudinal modes of vibration are present, but the transverse modes cannot exist. Hence the total number of modes of vibration should be equal to just the total number of particles in the liquid. If we do Franchetti's calculation, by calculating the cutoff frequency from the condition that the total number of modes of vibration is just equal to  $N$ , then we obtain approximately

$$Z(d) \approx Z(\infty) \left[ 1 + \frac{1}{33.7} \left( \frac{c}{d\gamma_{\infty}^c} \right)^2 + \dots \right] , \quad (7.20)$$

which is now in good agreement with Eq. (7.12).





## CHAPTER 8

### CONCLUSION

In this thesis we have, in the first place, extended the quantum mechanical theory of surface tension proposed by Atkins, which considers the free energy contribution of quantized surface modes of vibration as an essential part of the surface tension of a quantum liquid. We have shown moreover that the surface correction to the free energy of bulk liquid excitations - phonons and rotons - is much smaller than the free energy of these quantized surface modes, or ripplons.

Our main contribution to this theory of the surface tension of liquid helium was, however, to calculate the intrinsic surface tension of liquid helium at  $T = 0^\circ\text{K}$ . This contribution to the surface tension was calculated on the basis of the imperfect-gas model of Gross and Pitaevski; this imperfect-gas model is able to give a description of the density non-uniformity at the <sup>free surface of the</sup> liquid, provided one assumes an attractive interaction between the atoms in the surface region. Consequently, one calculates the free energy per unit area associated with this non-uniformity and identifies this with the intrinsic surface tension of the liquid.

A test for the validity of this theory of the surface tension of a quantum liquid has been developed in Chapter 4. The two rival theories of surface tension give significantly different predictions for the interfacial surface tension of a phase-separated  $\text{He}^3\text{-He}^4$  system at  $T = 0^\circ\text{K}$ . An extrapolation of experimental measurements on the interfacial surface tension of



a  $\text{He}^3$ - $\text{He}^4$  system should be able to decide the issue between the two estimates.

In Chapter 5 we have demonstrated "qualitatively" the necessity of taking into account surface phenomena when discussing the lambda temperature depression in helium films. The criterion that we have used to define a lambda temperature was to compare the free energy of all excitations present in a helium film (including surface excitations) to the free energy of the excitations in bulk liquid helium. Clearly, since ripplons contribute to the free energy of the film, a lambda temperature depression will be observed, which depends on the film thickness. We have obtained reasonable agreement with results obtained from specific heat measurements, although the criterion that we have used to define the lambda temperature is not one that can be directly compared to experimental results.

In Chapter 6 we have calculated the lambda temperature depression that one might expect in rotating helium II. Rather than calculate the decrease in the superfluid density as a function of the angular velocity and the size of the rotating cylinder as was done approximately by Andronikashvili, Mamaladze and others, we have calculated the increase in the normal fluid density as a function of these parameters; this problem can be solved much more easily and surprisingly enough, the more general result obtained reduces to those obtained by Andronikashvili et al in the limit in which the lambda temperature depression depends on either the angular velocity or the size of the container alone.



In Chapter 7 we have presented some theoretical justification for Pathria's contention that the error term in the density of states formula (2.6) is, for the systems that we have considered, much inferior to the surface term. However, none of the results obtained in this thesis depend critically upon this contention.

The main criticism to be made of the above thesis, and of much of the previous work on liquid helium is that the results are generally based on macroscopic theories with little or no basis in microscopic theory. The main reason why microscopic theories have not been as successful in this field as in the field of superconductivity is, of course, that helium II is a liquid. Consequently, even a microscopic theory such as the hard-sphere Bose gas cannot be expected to account quantitatively or even qualitatively for many phenomena in helium II, especially those that are associated with the free surface, or with helium II films. A proper microscopic theory must take into account both the repulsive and attractive nature of the interparticle interaction in order to explain without ambiguity the phenomena occurring in liquid helium II.





## APPENDIX I

### FREE ENERGY OF A GAS OF NON-INTERACTING BOSE PARTICLES

We derive here expression (2.28) without replacing the summation over states by an integration; accordingly, we shall not make use of any explicit formula for  $g(K)$ . Let us consider a gas of noninteracting particles, each of mass  $m$ , confined to a volume  $V$ , which for simplicity is taken to be a cube of side  $a$ . The energies of the stationary states of any one particle are given by

$$\epsilon = (h^2/8ma^2) (s^2 + t^2 + u^2), \quad (\text{I-1})$$

where  $s$ ,  $t$ , and  $u$  can take only positive integral values in the case of the Dirichlet boundary condition, but can also take the value zero in the case of the Neumann boundary condition.

We then have for the logarithm of the grand partition function

$$\ln \mathcal{Q} = \sum_{s,t,u} \ln [1 - ze^{-\mu(s^2+t^2+u^2)}], \quad (\text{I-2})$$

where  $\mu = h^2/(8ma^2kT)$  and  $z$  is the fugacity of the system. The internal energy  $U$  can then be determined by the relationship

$$U = - \left[ \partial \log \mathcal{Q} / \partial \beta \right]_{zV}, \quad (\text{I-3})$$

where  $\beta = 1/kT$ . Carrying out the expansion (I-1) in powers of  $z$  and the differentiation as required by (I-2) we obtain





$$\begin{aligned}
 U &= \frac{h^2}{8ma^2} \sum_{s,t,u} \sum_{j=1}^{\infty} z^j (s^2+t^2+u^2) e^{-\mu j (s^2+t^2+u^2)} \\
 &\equiv \frac{3h^2}{8ma^2} \sum_{j=1}^{\infty} z^j \left[ \sum_s s^2 e^{-\mu j s^2} \right] \left[ \sum_t e^{-\mu j t^2} \right]^2. \quad (I-4)
 \end{aligned}$$

The sums involved here can be evaluated by using Poisson's formula

$$\sum_{s=-\infty}^{\infty} e^{-\mu j s^2} = \left( \frac{\pi}{\mu j} \right)^{1/2} \sum_{s=-\infty}^{\infty} e^{-\pi^2 s^2 / \mu j}, \quad (I-5)$$

and the one resulting from (I-5) by a differentiation with respect to  $(\mu j)$ , namely,

$$\sum_{s=-\infty}^{\infty} s^2 e^{-\mu j s^2} = \left( \frac{\pi}{(\mu j)^3} \right)^{1/2} \sum_{s=-\infty}^{\infty} \left[ \frac{1}{2} - \frac{\pi^2 s^2}{\mu j} \right] e^{-\pi^2 s^2 / \mu j}. \quad (I-6)$$

From (I-5) and (I-6) it follows that, in the limit  $\mu \rightarrow 0$ ,

$$\begin{aligned}
 \sum_{s=1}^{\infty} e^{-\mu j s^2} &\equiv \frac{1}{2} \left[ \left( \frac{\pi}{\mu j} \right)^{1/2} \sum_{s=-\infty}^{\infty} e^{-\pi^2 s^2 / \mu j} - 1 \right] \\
 &\approx \frac{1}{2} \left[ (\pi / \mu j)^{1/2} - 1 \right], \quad (I-5^1)
 \end{aligned}$$

and

$$\sum_{s=1}^{\infty} s^2 e^{-\mu j s^2} \equiv \frac{1}{2} \sum_{s=-\infty}^{\infty} s^2 e^{-\mu j s^2} \approx \frac{1}{4} \left[ \pi / (\mu j)^3 \right]^{1/2}. \quad (I-6^1)$$



Accordingly, (I-4) becomes

$$U \approx \frac{3}{2} (V/\lambda^3) kT g_{5/2}(z) - \frac{1}{4} (A/\lambda^2) kT g_2(z), \quad (I-7)$$

where  $\lambda = h/(2\pi mkT)^{1/2}$  and the function

$$g_n(z) = \sum_{j=1}^{\infty} j^{-n} z^j.$$

The free energy of the system can be calculated by means of the formula

$$F = -T \int_0^T \frac{U}{T^2} dT, \quad (I-8)$$

whence we finally get

$$F = (-V/\lambda^3) kT g_{5/2}(z) - \frac{1}{4} (A/\lambda^2) kT g_2(z). \quad (I-9)$$

For  $T < T_\lambda$ ,  $z \approx 1$ ; then, for  $n > 1$ ,  $g_n(z) \approx \zeta(n)$ . The second term in (I-9) thereby gives precisely the expression (2.28) for  $F_s/A$ .



## APPENDIX II

### FREE ENERGY DUE TO NON-UNIFORMITY AT WALL

In order to calculate the free energy due to the interaction between the helium atoms and the rigid wall, we assume that, due to the short-range van der Waals forces, the density distribution of the film as a function of the distance from the wall is of the form depicted in Figure 1.

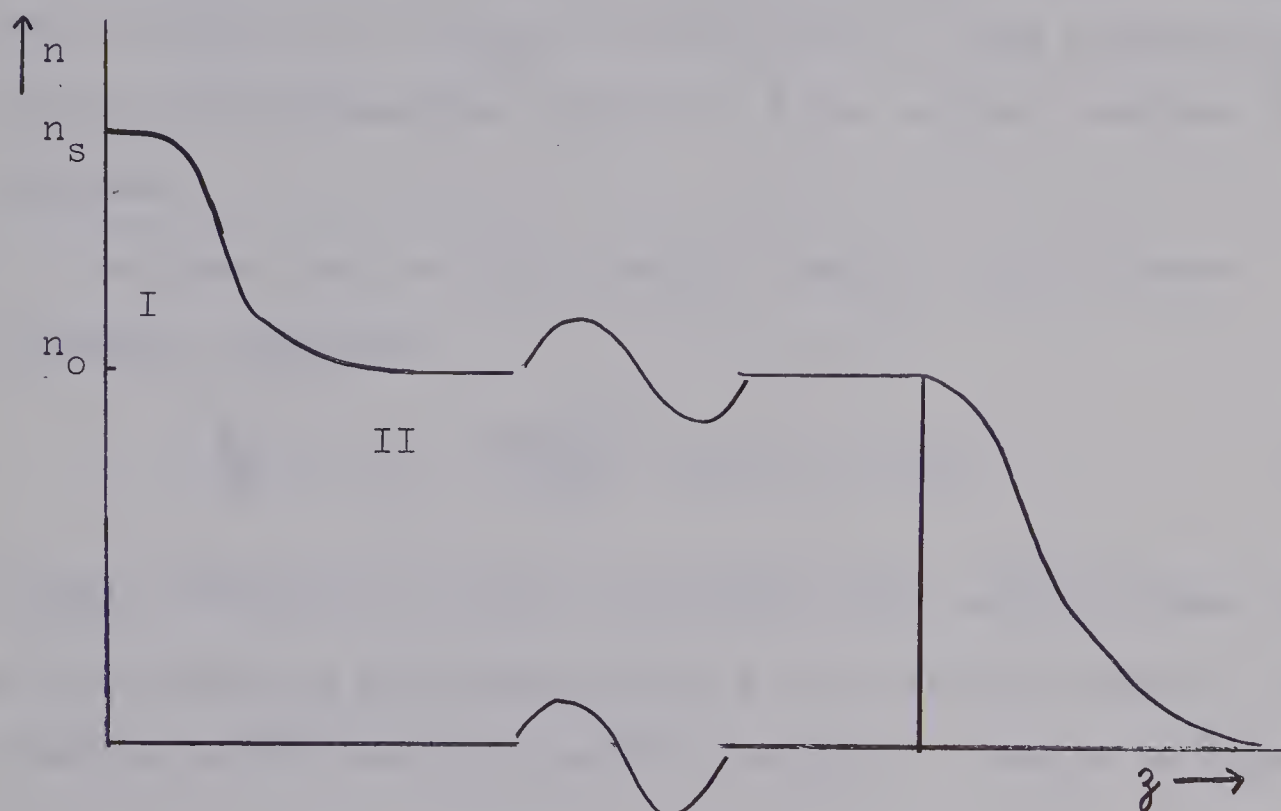


Fig. 1 Variation of superfluid density with  $z$  distance from the wall.

At present, it is impossible to take into account the precise nature of the van der Waals interaction and calculate the density nonuniformity and hence the free energy therefrom. Rather than take into account this interaction directly, let us solve a problem giving a similar density non-uniformity. We shall adopt a model in which the transition region I is a region





of density variation between a hypothetical high density phase of helium II and a low density phase of helium II. The density of the liquid in region I, extending in the negative z region, is given by the experimentally determined density  $n_s$  of the first layer of helium II from the wall. This density determines, or is determined by, the nature of the wall and the van der Waals interaction; hence the solution of this hypothetical problem determines the solution of the actual problem of interest.

We describe the high density region I by a Gross-Pitaevski equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_1 - \frac{4\pi|a|\hbar^2}{m} |\psi_1|^2 \psi_1 = \mu \psi_1. \quad (\text{II-1})$$

In this situation we let  $\mu$  represent the energy change that arises when one particle from the low density region II is transferred to the high density region I. Hence we have

$$\mu = \frac{-4\pi|a|\hbar^2}{m} |\psi_1(0)|^2 = \frac{-4\pi|a|\hbar^2}{m} (n_s - n_0). \quad (\text{II-2})$$

Thus the square of the wave function  $\psi_1$  represents the difference in density between region I and region II. The solution of Eq. (II-1) can be obtained analogous to the solution of equation (3.9). One again defined dimensionless parameters and obtains the solution

$$\psi_1 = \sqrt{n_s - n_0} \operatorname{sech}\left(\frac{x}{\ell}\right),$$



where

$$\ell = \frac{1}{\sqrt{4\pi|a|(n_s - n_o)}}.$$

At any point in the transition region then we have

$$n(x) = n_o + (n_s - n_o) \operatorname{sech}^2\left(\frac{x}{\ell}\right). \quad (\text{II.3})$$

If we compare this with the corresponding solution due to Cahn and Hilliard (3-22), we obtain a density distribution which is more or less similar. These authors obtained for a transition region between two phases of a classical fluid

$$n(x) = n_o + (n_s - n_o) \tanh\left(\frac{x}{\ell}\right). \quad (\text{II.4})$$

Again, as before, we can calculate the free energy due to such a density non-uniformity and obtain the result

$$\frac{F - F_o}{A} = \frac{1}{3} \frac{\hbar^2 (n_s - n_o)}{m \ell} \quad (\text{II.5})$$

In order to obtain a numerical estimate for this energy we must again estimate the value of the scattering length  $a$ . Since we are using the experimentally determined surface tension which corresponds to a scattering length  $a = -4\text{\AA}$ , we use the same value here. We thus obtain

$$\frac{F - F_o}{A} = 0.092 \text{ erg cm}^{-2}. \quad (\text{II.6})$$

In the region of density non-uniformity near the wall, excitations will be created as the temperature is raised above



0°K, and will reduce the "effective" free energy. If we assume that the temperature variation of this free energy is the same as that of the surface free energy, we obtain for the temperature dependence of the free energy due to the non-uniformity at the wall,

$$\frac{F-F_0}{A} = 0.092 - 0.002 T^{2.5} \text{ erg cm}^{-2} \quad , \quad (\text{II.7})$$



# APPENDIX III

## INERTIAL DENSITY OF RIPPLONS

In order to calculate the inertial density of a two-dimensional gas of ripplons we again have to take the main term in the expression for the density of states (2.11) with  $n=2$ . We give the gas a drift velocity  $\underline{v}$  and calculate the drift momentum  $\underline{J}$ . The drift momentum of such a two-dimensional gas of excitations is thus

$$\underline{J} = \frac{A}{h^2} \int n(\epsilon - \underline{v} \cdot \underline{p}) p_z d^2p \quad . \quad (\text{III-1})$$

Applying the Taylor series expansion (6.7) for  $n(\epsilon - \underline{v} \cdot \underline{p})$ , the first term of the integral for the inertial density  $\rho_n$  of the ripplons becomes

$$\rho_n = \frac{J}{vV} = \frac{2\pi}{h^2 t} \int \frac{\partial n(\epsilon)}{\partial \epsilon} p^3 dp \quad . \quad (\text{III-2})$$

Using the energy-momentum relation  $\epsilon_p = \left(\frac{\sigma}{\hbar\rho}\right)^{1/2} p^{3/2}$  for ripplons, and substituting into Eq. (III-2) the expression

$$\frac{\partial n(\epsilon)}{\partial \epsilon} = \frac{2}{3} \left(\frac{\hbar\rho}{\sigma}\right)^{1/2} \frac{1}{p^{1/2}} \frac{\partial n(p)}{\partial p} \quad ,$$

we obtain

$$\rho_n = \frac{5\pi}{3h^2 t} \cdot \left(\frac{\hbar\rho}{\sigma}\right)^{1/2} \int n(p) p^{3/2} dp. \quad (\text{III-3})$$

Letting  $y = Ap^{3/2}$ , where  $A = \frac{1}{kT} \left(\frac{\sigma}{\hbar\rho}\right)^{1/2} p^{3/2}$ , we substitute for the occupation number of a gas of ripplons the expression  $n(p) = (\exp Ap^{3/2} - 1)^{-1}$  and obtain the result

$$\rho_n = \frac{10\pi}{9h^2 t} A^{-2/3} \int \frac{y^{3/2}}{e^y - 1} dy \quad .$$

This expression can be evaluated in terms of the Riemann Zeta function to yield

$$\rho_n = \frac{10\pi}{9h^2 t} \left(\frac{\hbar\rho}{\sigma}\right)^{4/3} \Gamma(5/3) \zeta(5/3) (kT)^{5/3}. \quad (\text{III.4})$$





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